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## Review

# Structural Chemistry of Borophosphates, Metalloborophosphates, and Related Compounds

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*Dedicated to Professor Brigitte Eisenmann on the Occasion of her 65th Birthday*

**Abstract.** A concept for the classification of crystalline (metallo)-borophosphates in terms of structural chemistry is proposed and the compounds known to date are classified in an overview. Similarities and differences with (alumo)silicates and *Liebau's* classification are discussed with respect to the observation that the different borate and phosphate complexes are not interconnected arbitrarily in borophosphates. By combination and extension of existing concepts for silicates and borates a hierarchical system based on oligomeric building units has been developed. The observed connection rules are rationalized and the strong influence of the composition on dimensionality and structural motifs of the formed anions is

pointed out. Likewise the effect of OH groups is taken into account by grading anions according to the degree of protonation (ratio O:OH). A general distinction is made between tetrahedral and mixed coordinated borophosphates. Metalloborophosphates are treated separately as special cases of borophosphates. Finally, anion-substituted compounds, border cases, and borate-phosphates complete the overview.

**Keywords:** Borophosphates; Metalloborophosphates; Structural chemistry

## Introduction

With the systematic research on crystalline borophosphates which started just 12 years back [1] a large number of new compounds has been reported, dense structures as well as microporous frameworks and templated solids hosting template cations or molecules. Borophosphates comprise an exciting structural chemistry with a great variety of connection patterns and variable extension of the anionic partial structures – a structural chemistry similar to (alumo)silicates [2]. In all these structures, although comprising a large range of borate to phosphate units (B:P ratio), certain ratios seem to be preferred and some anionic partial structures and connection patterns are found more frequently than others.

As the number of compounds grew steadily since the first approach to this topic in 1997 [3] borophosphates necessarily have to be reviewed again on the basis of a deeper insight into structural chemistry. A systematic classification is pro-

posed which considers the composition of the anions as well as the different connection patterns. It is based on the description for (alumo)silicates introduced by *Liebau* and a hierarchical classification by building units following the principle ideas of a concept introduced for borates [4, 5]. A similar classification by building blocks has already been applied but on a small series of borophosphates only [6]. Here, all borophosphates, metalloborophosphates, and borate-phosphates known to date are presented and are systematically assorted in terms of an overview. Anion-substituted compounds and special cases not fitting the given definition of borophosphates are likewise summarized and discussed. As mentioned in the beginning, this work is exclusively focused on crystalline phases. Structural investigations on borophosphate glasses are presented in recent publications [7, 8].

## 2 Fundamentals

The close structural relationship of boron phosphate and SiO<sub>2</sub> was known since the first structural investigations by *Schulze* in 1934 [9] which proved BPO<sub>4</sub> to be a III/V-heterotype quartz variant (isoelectronic BPO<sub>4</sub> ↔ “SiSiO<sub>4</sub>”) with β-cristobalite modification. Nevertheless, research was mainly focused on the catalytic properties and the formation of high-pressure phases of BPO<sub>4</sub> (α-quartz modifi-

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cation) as summarized in [10], neglecting the corresponding borophosphates (in contrast to systems with the boron homologues Al and Ga). Boron phosphate itself will not be part of this review as it bases on a classification of anionic partial structures.

The notations borophosphates and metalloborophosphates are trivial names, thus, a proper definition and some fundamental rules have to be given to define the scope of this work. Commonly borophosphates are denoted as intermediate compounds of systems  $M_xO_y-B_2O_3-P_2O_5(-H_2O)$  ( $M$  = main-group/transition metal, ammonium). Additionally, organic molecules/cations (mainly amines) play an important role in the synthesis of open-framework structures. The group of borophosphates will be limited to compounds with boron in oxidation state +3 and phosphorus in oxidation state +5, both exclusively coordinated by oxygen and OH-groups (substituted variants will be discussed separately). At least one borate and one phosphate unit have to be condensed to form a borophosphate.

Following the IUPAC rules of nomenclature [11, 12], the systematic names of borophosphates have to be formed from the names of the participating complex anions which contain the information about the central atom, the ligands, and the resulting charge. Identical ligands are counted with a multiplier prefix (mono-, di-, tri-, ...). Thus, a  $[PO_4]^{3-}$  anion is denoted as [Tetraoxophosphate(3-)], a  $[BO_3]^{3-}$  anion as [Trioxoborate(3-)], and a  $[BO_4]^{5-}$  anion as [Tetraoxoborate(5-)]. Adding the sequences pointing out bridging ligands and acid hydrogen atoms attached to the polyanion together with the additional multipliers for identical complex assemblies (Bis-, Tris-, Tetrakis-,...), the names rapidly turn out to be very complex. This notation may be formally correct but does not necessarily contribute to comprehension. For heteropolyanions like borophosphates, and even more for metalloborophosphates, where additional tetrahedral units are present in the anionic partial structures, the use of trivial-names can be helpful. This is widely accepted e.g. for "alumosilicates", "borosilicates" or "alumophosphates". Thus, the use of the expressions "borophosphate(s)" and "metalloborophosphate(s)" as well as the resulting semi-trivial systematic notation is not only reasonable, but also accepted according to the IUPAC rec-

ommendations [12]. Occasionally borophosphates are denoted as borate-phosphates, this is neither in accordance with the IUPAC recommendations nor a reasonable trivial nomenclature as the presence of isolated borate and phosphate anions is suggested. In this work it will clearly be distinguished between borophosphates and borate-phosphates.

Whereas phosphorus in oxidation state +5 is always four-fold coordinated, boron can be surrounded by three or four oxygen atoms. Thus, the construction set of borophosphates consist of trigonal-planar  $B\Phi_3$  and tetrahedral  $B\Phi_4$  and  $P\Phi_4$  specimens, non-protonated and protonated ( $\Phi = O, OH$ ). These complex anions are exclusively linked via common corners to form oligomers (by definition at least one borate and one phosphate group), chains, layers, and frameworks. In all those various structures, comprising many different structural motifs, the connections between building units are not arbitrary. P–O–P connections have not been observed within the borophosphate anions up to date.<sup>1)</sup> Thus, borophosphate anions with B:P ratios lower than 1:4 have not been found and additional phosphate units – isolated or condensed – remain isolated in the crystal structures. This avoidance of P–O–P connections reminds of the situation in alumosilicates where Al–O–Al bonds in tetrahedral arrangements are (mostly) avoided (*Loewenstein* rule) [13] and it indicates that such a rule could be valid for borophosphates as well. In case of borophosphates a possible explanation for missing P–O–P connections can be found in *Paulings* fourth rule [14] which means, that in a crystal containing different cations, those of high charge and low coordination number tend not to share these polyhedra with one another. This rule is in good agreement with the observations that for increased phosphate content the phosphate groups in borophosphates take terminal positions, that the dimensionality of borophosphate anions decreases and that even isolated phosphate groups appear.

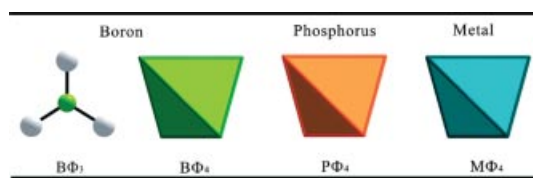
If borate and phosphate units are isolated in the crystal structure, the compounds are not called borophosphates but borate-phosphates. These are not part of the structural systematics but will be presented separately just for completeness. Metalloborophosphates additionally contain tetrahedral  $M\Phi_4$  building units in the condensed anions. Metal complexes with coordination numbers other (greater) than four (non-tetrahedral coordination), are not counted as part of the anionic partial structure. A summary of all building units in borophosphates and metalloborophosphates with the color-coding used in this work is given in Figure 1.

In order to preserve certain continuity the nomenclature and structural systematic were chosen as close as possible to a first approach to borophosphate structural chemistry published by *Kniep et al.* [3] and the nomenclature for sili-

<sup>1)</sup> Nevertheless, condensed phosphates may exist besides a borophosphate anion.

#### General symbols and abbreviations.

*(in figures)	Building unit also exists as isolated anion in borophosphates (oligomer)
BPO / MBPO	Borophosphate / Metalloborophosphate
FBU	Fundamental Building Units
BBU	Basic Building Units
SG	Space Group
Synth.	Synthesis method
H	Hydrothermal synthesis
S	Solid state synthesis
ST	Solvothermal synthesis
O	Synthesized in open systems (aqueous media, not hydrothermal)
N	Natural mineral
F	Synthesized using a flux



**Fig 1** Coordination polyhedra and color coding in the construction set of (metallo-)borophosphates ( $\Phi = \text{O}, \text{OH}$ ).

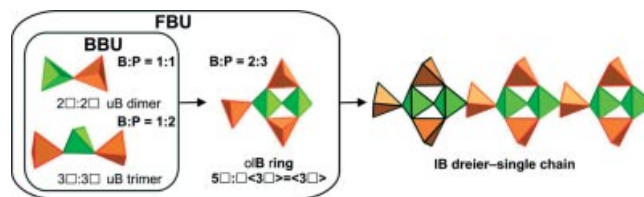
catates presented by *Liebau* [2]. Nevertheless, a detailed comparison with the structural chemistry of borates [4, 5] and phosphates [15, 16] is essential. As stated above, we are dealing with heterotypic arrangements and the composition has a strong influence on the dimensionality of the anionic partial structures. Thus, the ratio of borate to phosphate units (B:P) is an important classification criterion for borophosphates. Likewise, the quota of metal centered tetrahedra in metalloborophosphates is taken into account with the parameter  $M:B:P$ . Whereas the structural chemistry of silicates mainly comprises tetrahedral building units ( $CN = 4$ ), (metallo)borophosphates can contain trigonal planar  $B\Phi_3$  groups as well and structural patterns may occur that are only known from borate structures [4, 5]. Thus, classification concepts developed for silicates and borates are applied to describe and hierarchically assort the existing (metallo)borophosphate anions.

In contrast to the first approach to borophosphate structural chemistry [3], the anionic arrangements are divided into “tetrahedral” and “mixed coordinated”; metalloborophosphates (hitherto purely tetrahedral) are treated separately. Disassembled into fundamental building units (representative oligomeric fragments), the anions are further graded according to their B:P ratio and their degree of protonation (O:OH). This scheme makes it possible to assort the (metallo)borophosphates hierarchically and all compounds in one branch of this hierarchy have common structural motifs and, thus, can be referred to the same fundamental and basic building units. If available, space groups and methods of preparation are given as additional information for all the phases. In this way the overview of existing compounds presented in the following may not only be used as a database but also as a helpful tool for synthetic strategies to prepare crystalline borophosphates.

### 3 Classification Scheme

Borophosphates are first divided into purely tetrahedral and mixed coordinated partial structures, thus, the coordination number ( $CN$ ) of boron is already an important characteristic for the classification. This differentiation appears to be useful as different structural patterns are formed. Metalloborophosphates are exclusively built of tetrahedra. In order to treat borophosphates as heterotypes of phosphates and borates, the ratio of borate to phosphate building units is one of the most important criteria of classification, especially as it has a strong influence on the dimen-

sionality of the anions. Due to the avoidance of P–O–P bonds, the B:P ratio and the dimensionality are limited for phosphate rich anions ( $B:P \leq 1:1$ ) and phosphate groups occupy terminal positions. For borate rich phases (hitherto only mixed coordinated) a limitation of the dimensionality to  $D = 1$  is observed. The B:P ratio exclusively considers the structural elements of the borophosphate anion, isolated borate and phosphate groups are not counted. If two different anionic entities are present, the more complex one should be chosen for classification (though not observed to date). For further classification the anionic partial structures are disassembled into their fundamental building units (FBUs) as proposed in a similar fashion for borates [4, 5]. The FBU is a representative oligomeric fragment of the anion and contains the essential structural motifs (in the case of oligomers the FBU can be identical with the complex anion). The most primitive building units – short oligomers with simple B:P ratios, mostly unbranched or open-branched – determine the composition of the anion and are called basic building units (BBUs) as the more complex FBUs can be created from these. Depending on which BBUs are taking part in the structure formation and how they are condensed, FBUs with different structural patterns and different B:P ratios are formed. This concept is shown in Figure 2 where a borophosphate chain (B:P = 2:3) is constructed from its BBUs (B:P = 1:1 and 1:2).

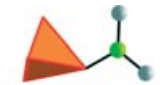






**Fig. 2** Construction of a borophosphate chain starting from BBUs. The FBU is highlighted with black edges in the chain (right). For explanation of descriptors and symbols see Tables 1 and 2 in the following.

Fundamental building units can be illustrated with a descriptor of two strings of the type A:B where string A gives the number of participating polyhedra and string B contains the information of the connection (the structural pattern) [4, 5]. In this illustration every tetrahedron is represented as  $\square$  and trigonal planar units as  $\Delta$ . Any sequence of these symbols (string B) corresponds with a linear sequence of polyhedra linked via common vertices. Further symbols (delimiters) are necessary to describe the existence of branches or rings. Polyhedra forming ring motifs are enclosed by  $\langle \dots \rangle$ , central units in a branching are delimited by  $[ \dots ]$  and all attached branches are separated by  $|$ . In some structural patterns two motifs comprise shared polyhedra, the number of common polyhedra is then indicated by horizontal lines ( $-$ ,  $=$ ,  $\equiv$ ...). A summary of the symbols used is given in Table 1, together with some examples with complete descriptors (bottom).

All borophosphates that can be referred to the same FBU are then graded due to their dimensionality in the order

**Table 1** Symbols used in descriptors as well as some simple examples.

Symbol	Description
$\square$	tetrahedron ( $B\Phi_4$ , $P\Phi_4$ , $M\Phi_4$ )
$\Delta$	trigonal planar ( $B\Phi_3$ )
$\langle \dots \rangle$	ring motif
$[\dots]$	branching polyhedron/anion
–, =, ≡, ...	separator for branches structural motifs share 1, 2, 3, ... common polyhedra
Examples	Descriptor A:B
	$\square\Delta:\square\Delta$ (dimer)
	$3\square:3\square$ (uB trimer)
	$4\square:[\square]\square[\square]$ (oB tetramer)
	$6\square:\langle 6\square \rangle$ (uB ring)
	$6\square:[\langle 3\square \rangle]=\langle 3\square \rangle[\square]$ (oIB ring)

from oligomers to three dimensional frameworks ( $D = 0, 1, 2, 3$ ) and their degree of protonation (O:OH). By this way of classification all borophosphates with the same B:P ratio are grouped and assorted in branches with common FBUs.

As widely accepted, the description of the borophosphate anions is made in accordance with the terminology for silicates [2] with just some minor modifications. The coordination number  $CN$  is an important factor in the classification as it divides borophosphates in “tetrahedral” and “mixed coordinated” anions. In borophosphates only vertex connections between the polyhedral building units is observed, thus, the parameter linkedness ( $L$ , number of shared oxygen atoms in a connection) is obsolete. All terms and parameters used to describe borophosphate anions are summarized in Table 2 and will be explained in the following.

The parameter connectedness  $Q^{n/CN}$  gives the number  $n$  of polyhedra a focused polyhedron ( $Q = B, P, M$ ) is connected to. As in borophosphates connections are only made via common vertices, this number complies with the number of shared oxygen atoms. In order to distinguish between tetrahedral and trigonal planar building units, the coordination number  $CN$  is added. Like this, terminal („primary“,  $Q^{1/CN}$ ), linearly connecting („secondary“,  $Q^{2/CN}$ ) or branch-

**Table 2** Parameters for the description of borophosphate anions, derived from the classification concept for silicates by *Liebau*.

Parameter	Value, description
Coordination number	$CN = 3$ (boron), 4
Connectedness	$Q^{n/CN} = B, P, M$ $n =$ number of connections
Branchedness <sup>a)</sup>	$B =$ uB, oB, lB, cB, hB (unbranched, open-, loop-, cyclo-branched) Mixed Branching: $B =$ oIB, ocB, clB, ...
Dimensionality	$D = 0, 0(r), 1, 1(tb), 2, 3$ oligomer, ring, chain, tube, layer, network
Multiplicity	$M = 1, 2, 3, \dots$ „single“, „double“, „triple“, ...
Periodicity <sup>b)</sup>	$P = 1, 2, 3, \dots$ „einer“, „zweier“, „dreier“, ...

<sup>a)</sup> Furthermore the term hybrid (hB) can be used if a branched anion is linked to an unbranched one.

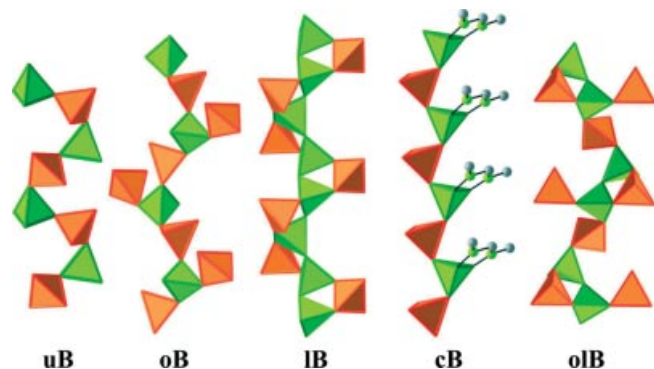
<sup>b)</sup> Likewise used to describe the size of rings ( $P \geq 3$ )

ing („tertiary“  $Q^{3/CN}$  and “quaternary“  $Q^{4/CN}$ ) polyhedra are easily qualified. Singular polyhedra ( $Q^{0/CN}$ ) disagree with the definition of borophosphates but can be found besides a borophosphate anion. If a structure just contains  $Q^{0/CN}$  units, it has to be classified as borate-phosphate.

The parameter branchedness ( $B$ ) allows describing the connection patterns of complex anions which deviate from simple linear (unbranched) condensation. Various branchings are exemplified in Figure 3 for some chain anions, starting with an unbranched example (uB). If a branch is attached with only one vertex to the linear part of the anion, it is called open-branched (oB). As soon as a branch has two connections to the backbone it has to be differentiated between two cyclic motifs: cyclo-branches (cB) in which both ends of the branch are connected to the same polyhedron, and loop-branches (lB) which connect different polyhedra along the backbone. In the case that different types of branching are present, the general term “mixed-branched” is used, but all branchings are given in the descriptive sequence as shown for an open- and loop-branched chain (oIB).

The parameters dimensionality, multiplicity and periodicity were adopted without changes from the crystal chemical classification proposed for silicates [2] and are, thus, just briefly described. The dimensionality ( $D = 0, 1, 2, 3$ ) gives the extension of the anionic partial structure in the sequence oligomer, chain, layer (network) and framework. Cyclic oligomers (rings) do not contain terminal polyhedra in the unbranched part of the anion and are closely related to chains, thus, the dimensionality is marked as  $D = 0(r)$ . In the same way a tube is a special case of a chain (related to layers) and, thus, marked as  $D = 1(tb)$ . If a limited number of polyhedral assemblies (single chains, layers) are connected to multiple anions of the same dimensionality, the number of identical anions is given by the parameter multiplicity ( $M = 1, 2, 3, \dots$ ) and quantified with multipliers (single, double, triple, ...). In contrast to silicates oligomeric units are not denoted as multiple polyhedra (but as dimers,

trimers, ...) as isolated polyhedra are in contradiction with the definition of borophosphates. The periodicity  $P$  is defined as the number of polyhedra in the repetitive unit of the linear part of the chain, branches are not counted. To denote a chain anion according to its periodicity the German terms "einer, zweier, dreier, ..." for  $P = 1, 2, 3, \dots$  as proposed by *Liebau* [2] are widely accepted.



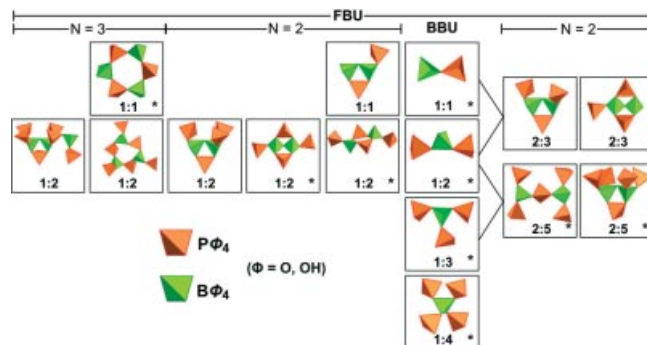
**Fig. 3** Different types of branching in borophosphates exemplified with simple chain anions. The notification is likewise valid for oligomers and rings. If different types of branching are present (mixed-branching) all are given in a sequence as shown for the open- and loop-branched chain to the right (olB).

## 4 Borophosphates – Overview

### 4.1 Tetrahedral borophosphates

The large majority of borophosphates comprises anionic arrangements that exclusively contain boron and phosphorus in tetrahedral coordination. These arrangements are hitherto only known with  $B:P \leq 1:1$  as with higher borate content  $B\Phi_3$  triangles are always present in the borophosphate partial structures. In the simplest case exactly one borate and one phosphate tetrahedron are condensed via a common oxygen vertex to form a dimer. Avoiding P–O–P connections oligomers with lower B:P ratios (1:2, 1:3, 1:4) can be obtained by attaching further phosphate tetrahedra to the central borate group until, finally, a fully branched pentamer results which comprises the lowest possible B:P ratio of 1:4. With exception of the latter one, these simple unbranched or open-branched oligomers (BBUs) may exist as isolated anions or can be condensed to extended partial structures (again avoiding P–O–P connections). In the next condensation step bigger oligomers (FBUs) with a retained or new B:P ratio are formed, depending on which and how many ( $N$ ) BBUs are combined. As a function of the number of oxygen atoms shared in the connections different structural motifs (branches, rings) result as shown in Figure 4. These arrangements of tetrahedra likewise exist as isolated anions in borophosphates (marked with \*), or are found as repetitive structural fragments when anionic partial structures of higher dimensionality (chains, layers, frameworks) are disassembled. Key feature is that a FBU

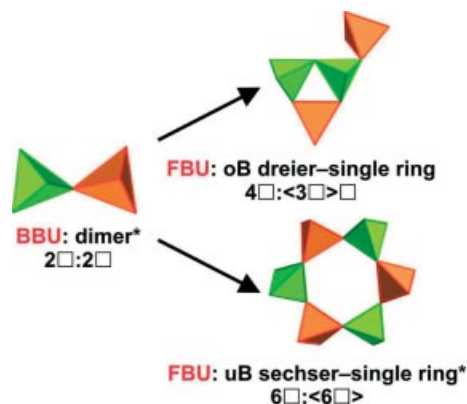
already contains the essential structural motif (and B:P ratio) of the resulting tetrahedral borophosphates.



**Fig. 4** Observed fundamental building units (FBUs) in tetrahedral borophosphates generated from a set of basic building units (BBUs). Depending on which and how many ( $N$ ) BBUs are condensed FBUs with different B:P ratios are formed. The number of oxygen atoms shared by condensation decides about the structural motif (rings, branches). FBUs/BBUs which exist as isolated anions are marked with an asterisk.

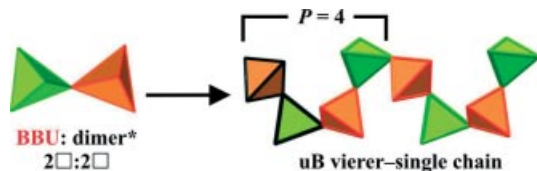
### B:P = 1:1

The structural hierarchy of tetrahedral borophosphates with a ratio  $B:P = 1:1$  is based on the most simple building unit: a dimer  $[BP\Phi_7]$  ( $\Phi = O, OH$ ) which is described by the sequence  $2\Box:2\Box$ . In the first level of hierarchy only an open-branched three-membered ring  $4\Box:<3\Box>\Box$  and an unbranched six-membered ring  $6\Box:6\Box$  are known as fundamental building units. These can be constructed by condensation of two and three of the BBUs, respectively (Fig. 5). Whereas the dimer and the six-membered ring exist as well as isolated anions in borophosphates, the oB dreier-single ring is exclusively found as a fragment of anionic partial structures with higher dimensionality.



**Fig. 5** Fundamental building units found in the first hierarchy level of tetrahedral borophosphates with  $B:P = 1:1$ . An open-branched three-membered ring and an unbranched six-membered ring can be formed by condensation of two and three BBUs, respectively.

**Borophosphates based on  $2\text{BO}_2$ .** The number of borophosphates which can only be referred to the basic dimeric building unit  $2\text{BO}_2$  is small. Besides the trivial case that the anionic partial structure is identical with the dimer, unbranched single chains are known resulting from linear condensation of the BBU (Fig. 6).



**Fig. 6** Unbranched chains of tetrahedra in borophosphates with B:P = 1:1 formed by linear condensation of  $[\text{BP}\Phi_7]$  dimers ( $2\text{BO}_2$ ).

All crystal structures known so far in this branch are summarized in Table 3. The only example comprising dimeric anions is the natural mineral Lüneburgite,  $\text{Mg}_3(\text{H}_2\text{O})_6[\text{BPO}_4(\text{OH})_3]$ . Two different types of borophosphates exist containing unbranched vierer-single chains  ${}_{\infty}^1[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5^{3-}]$  built of alternating borate and phosphate tetrahedra:  $M^{\text{III}}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$  ( $M^{\text{III}} = \text{Fe, Ga}$ ) and  $\text{Al}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5] \cdot \text{H}_2\text{O}$ . Whereas the iron and gallium borophosphate are isotypes, the crystal structure of the aluminum phase differs in the presence of hydrate water. Furthermore, three isotopic chiral phases  $M^{\text{II}}[\text{BPO}_4(\text{OH})_2]$  ( $M^{\text{III}} = \text{Mn, Fe, Co}$ ) have been reported. Striking feature of these structures is the arrangement of the borophosphate chains in three different directions (layerwise rotated by  $60^\circ$ ).

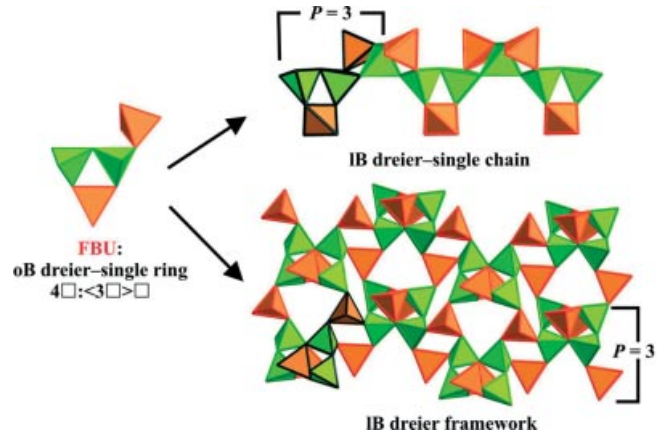
All compounds in this branch, Lüneburgite as well as the chain-borophosphates, comprise protonated anionic partial structures and can be synthesized from aqueous media, either hydrothermally (H) or from concentrated solutions in an open system as described for “synthetic” Lüneburgite (O).

**Table 3** Anionic partial structures referred to the dimeric BBU  $2\text{BO}_2$ .

Dimer $[\text{BP}\Phi_7]$ ( $\Phi = \text{O, OH}$ ) $D = 0; M = 1; Q^{\text{m/CN}}: \text{B}^{1/4}, \text{P}^{1/4}$				
O:OH	Compound	SG	Synth.	Ref.
4:3	$\text{Mg}_3(\text{H}_2\text{O})_6[\{\text{BPO}_4(\text{OH})_3\}_2]$	$P\bar{1}$ (No. 2)	N, O	[17, 18]
Chain ${}_{\infty}^1[\text{B}_2\text{P}_2\Phi_{12}]$ ( $\Phi = \text{O, OH}$ ) $D = 1; M = 1; Q^{\text{m/CN}}: \text{B}^{2/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
4:2	$M^{\text{II}}[\text{BPO}_4(\text{OH})_2]$ ( $M^{\text{II}} = \text{Mn, Fe, Co}$ )	$P3_21$ (No. 152)/ $P3_21$ (No. 154)	H	[19]
7:5	$M^{\text{III}}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ ( $M^{\text{III}} = \text{Fe, Ga}$ ) $\text{Al}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5] \cdot \text{H}_2\text{O}$	$C2/c$ (No.15)	H	[20, 21]
		$C2/c$ (No.15)	H	[22]

**Borophosphates based on  $4\text{BO}_2 < 3\text{BO}_2 >$ .** Avoiding bridging oxygen atoms between phosphate groups, two dimeric BBUs may be condensed via two common vertices forming an open-branched three-membered ring  $4\text{BO}_2 < 3\text{BO}_2 >$ . A

loop-branched chain motif and a loop-branched framework are known comprising this fragment  $[\text{B}_2\text{P}_2\Phi_{12}]$  as FBU. The different condensation schemes (linear or three-dimensional) of the FBU are shown in Figure 7, a summary of compounds reported so far in this hierarchical branch is given in Table 4.



**Fig. 7** Open-branched three-membered rings as fundamental building unit for partial structures of higher-dimensionality: By different condensation of the FBU a loop-branched dreier-single chain and a loop-branched dreier framework can be formed which are observed in borophosphates (see Tab. 4).

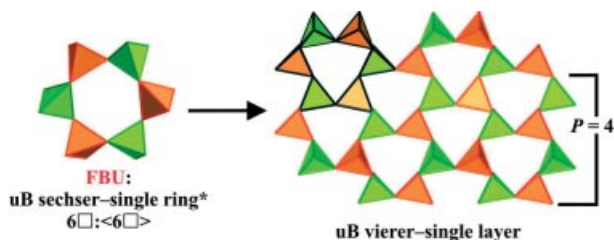
**Table 4** Borophosphates with B:P = 1:1 comprising the FBU  $4\text{BO}_2 < 3\text{BO}_2 >$ .

Chain ${}_{\infty}^1[\text{BP}\Phi_5]$ ( $\Phi = \text{O, OH}$ ) $D = 1; M = 1; Q^{\text{m/CN}}: \text{B}^{4/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
1:0	$M^{\text{II}}[\text{BPO}_5]$ ( $M^{\text{II}} = \text{Ca, Sr, Ba}$ ) $M^{\text{II}} = \text{Pb}$	$P3_21$ (No. 152)/ $P3_21$ (No. 154) hexagonal	S, F, H S	[1, 24–26] [27]
Framework ${}_{\infty}^3[\text{B}_2\text{P}_2\Phi_9]$ ( $\Phi = \text{O, OH}$ ) $D = 3; M = 1; Q^{\text{m/CN}}: \text{B}^{4/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
8:1	$M^{\text{I}}[\text{B}_2\text{P}_2\text{O}_8(\text{OH})]$ ( $M^{\text{I}} = \text{Rb, Cs}$ )	$P2_1/c$ (No. 14)	H	[28]

The borophosphates  $M^{\text{II}}[\text{BPO}_5]$  contain loop-branched dreier-single chains wound around a three-fold screw-axis and belong to the family of stillwellites (stillwellite:  $\text{Ce}[\text{B-SiO}_5]$  [23]). Different methods of preparation were applied, and the compounds were obtained by hydrothermal synthesis, solid-state reactions or flux-methods. Furthermore, the protonated loop-branched dreier-framework present in the two isotopic alkali-metal borophosphates  $M^{\text{I}}[\text{B}_2\text{P}_2\text{O}_8(\text{OH})]$  ( $M^{\text{I}} = \text{Rb, Cs}$ ) can be disassembled into loop-branched chains which are consistent with a linear condensation of FBUs  $4\text{BO}_2 < 3\text{BO}_2 >$ . Both compounds were obtained hydrothermally.

**Borophosphates based on  $6\text{BO}_2 < 6\text{BO}_2 >$ .** Unbranched six-membered rings of alternating borate and phosphate tetrahedra are found as isolated anions or as a building block

of unbranched layers with  $6^3$  net-topology (Fig. 8). In both cases the anionic partial structures are protonated. A summary of the compounds based on the six-membered ring FBU  $6\Box:\langle 6\Box\rangle$  is given in Table 5.



**Fig. 8** The unbranched six-membered ring FBU  $6\Box:\langle 6\Box\rangle$  exists as an isolated anion and condensed to form uB vierer-single layers with  $6^3$  net-topology.

**Table 5** Tetrahedral borophosphates built from unbranched six-membered ring FBUs  $6\Box:\langle 6\Box\rangle$ .

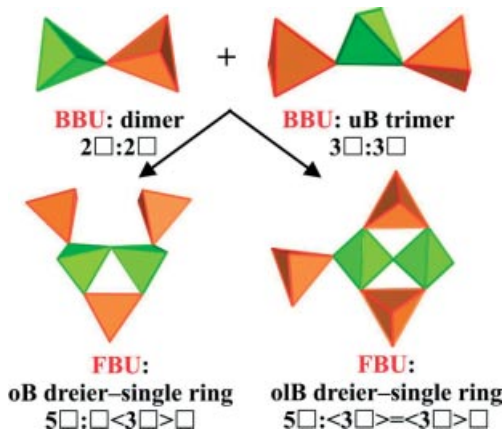
O:OH	Compound	uB rings $\frac{1}{2}[\text{BP}\Phi_6]_3$ ( $\Phi = \text{O, OH}$ ) $D = 0(r); M = 1; Q^{n/CN}: \text{B}^{3/4}, \text{P}^{2/4}$	SG	Synth.	Ref.
2:1	$M^{\text{II}}(\text{H}_2\text{O})_2[\text{BPO}_4(\text{OH})_2]$ $M^{\text{II}} = \text{Mg, Mg}_{1-x}\text{Ni}_x$ ( $x \approx 0.5$ )		$R\bar{3}c$ (No. 167)	H	[29, 30]
O:OH	Compound	uB layers $\frac{2}{3}[\text{B}_2\text{P}_2\Phi_{10}]$ ( $\Phi = \text{O, OH}$ ) $D = 2; M = 1; Q^{n/CN}: \text{B}^{3/4}, \text{P}^{3/4}$	SG	Synth.	Ref.
4:1	$\text{Cu}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]$ $M^{\text{II}}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ $M^{\text{II}} = \text{Mg, Mg}_{1-x}\text{Co}_x$ ( $x \approx 0.25$ )		$Pbca$ (No. 61) $P2_1/c$ (No. 14)	H	[31] [32, 33]

Only a small group of isotypic borophosphates  $M^{\text{II}}(\text{H}_2\text{O})_2[\text{BPO}_4(\text{OH})_2]$  comprises isolated unbranched six-membered rings. The anions are protonated and the compounds were synthesized hydrothermally. Likewise small is the number of known borophosphates containing the unbranched vierer-single layers  $\frac{2}{3}[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]$  ( $6^3$  net-topology). Only  $\text{Cu}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]$  and two isotypic compounds  $M(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$  ( $M = \text{Mg, Mg}_{1-x}\text{Co}_x$ ) have been reported so far, all comprising the same corrugated borophosphate layers in terms of composition and topology. Differences are found in the presence of hydrate water and the coordination sphere of the metal cations, resulting in a higher symmetry for the copper compound. The compounds under consideration were all synthesized under hydrothermal conditions.

### B:P = 2:3

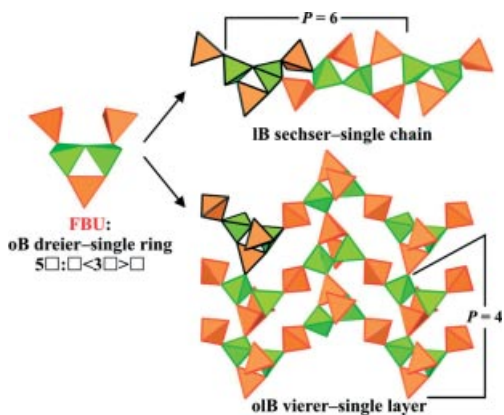
Fundamental building units with a B:P ratio of 2:3 can be generated by formal condensation of BBUs with B:P = 1:1 ( $2\Box:2\Box$ ) and B:P = 1:2 ( $3\Box:3\Box$ ) as shown in Fig. 9. A connection via two common vertices leads to the formation of an open-branched three-membered ring motif ( $5\Box:\square\langle 3\Box\rangle\square$ ). Mixed-branched three-membered rings ( $5\Box:\langle 3\Box\rangle=\langle 3\Box\rangle\square$ ) are observed if three oxygen posi-

tions are shared within the connection. None of the two pentameric FBUs exists as isolated anion in borophosphates. Both are exclusively found as fragments of higher-dimensional tetrahedral assemblies in which they are connected to one another avoiding common oxygen atoms between phosphate tetrahedra.



**Fig. 9** First hierarchy level of tetrahedral borophosphates with the molar ratio B:P = 2:3: Condensation of BBUs with B:P = 1:1 and B:P = 1:2 results in branched cyclic FBUs, which are present in higher-dimensional anionic partial structures (chains, layers).

**Borophosphates based on  $5\Box:\square\langle 3\Box\rangle\square$ .** The open-branched cyclic FBU  $5\Box:\square\langle 3\Box\rangle\square$  shows two non-connecting oxygen atoms, one at each borate tetrahedron ( $\text{B}^{3/4}$ ). Thus, it may be condensed to form extended anions. Loop-branched sechser-single chains  $\frac{1}{6}[\text{B}_2\text{P}_3\Phi_{13}]$  ( $\Phi = \text{O, OH}$ ) comprising three- and four-membered rings are found if the FBUs are connected to one another along the branching phosphate groups ( $\text{P}^{1/4}$ ) as shown in Fig. 10 (top right). Furthermore, oIB vierer-single layers are known in which the cyclic FBUs  $5\Box:\square\langle 3\Box\rangle\square$  are condensed involving the  $\text{P}^{2/4}$  tetrahedron in the ring and one of the branching  $\text{P}^{1/4}$  units (Fig. 10, bottom right). In this case eight-membered rings of tetrahedra result as additional structural pattern.



**Fig. 10** Condensation of the pentameric FBU  $5\Box:\square\langle 3\Box\rangle\square$  forming tetrahedral chains or layers which are present in the crystal structures of a number of known borophosphates with B:P = 2:3.

**Table 6** Anionic partial structures with B:P = 2:3 referred to open-branched cyclic FBUs  $5\Box:\langle 3\Box\rangle\Box$ .

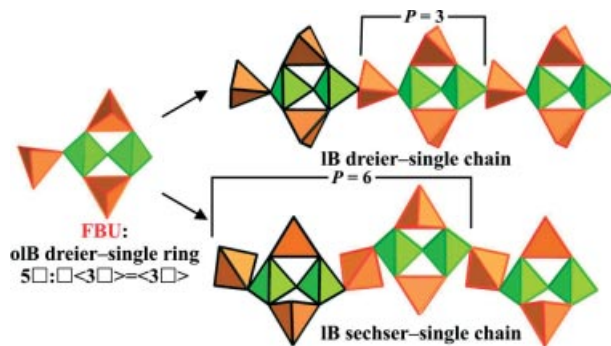
IB chains $\frac{1}{z}[\text{B}_2\text{P}_3\Phi_{13}]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 1; M = 1; Q^{n/CN}; \text{B}^{4/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
11:2	$[\text{Co}(\text{en})_3][\text{B}_2\text{P}_3\text{O}_{11}(\text{OH})_2]$ <i>C2/c</i> (No.15)	<i>C2/c</i> (No.15)	H	[34]
oIB layers $\frac{2}{z}[\text{B}_2\text{P}_3\Phi_{13}]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 2; M = 1; Q^{n/CN}; \text{B}^{3/4}, \text{P}^{1/4}, \text{P}^{3/4}$				
O:OH	Compound	SG	Synth.	Ref.
12:1	$\text{Rb}_2\text{Co}_3(\text{H}_2\text{O})_2[\text{B}_4\text{P}_6\text{O}_{24}(\text{OH})_2]$ $(\text{C}_2\text{H}_{10}\text{N}_2)\text{M}^{\text{II}}[\text{B}_2\text{P}_3\text{O}_{12}(\text{OH})]$ $\text{M}^{\text{II}} = \text{Mg}, \text{Mn-Zn}, \text{Cd}$	<i>Pbca</i> (No. 61)	H	[35]
	$(\text{C}_4\text{H}_{16}\text{N}_3)\text{Cd}[\text{B}_2\text{P}_3\text{O}_{12}(\text{OH})]\text{Cl}$	<i>Pbca</i> (No. 61)	H	[37]

A summary of borophosphates known so far in this hierarchical branch is given in Table 6. Whereas only one example has been reported to contain the loop-branched chain  $\frac{1}{z}[\text{B}_2\text{P}_3\Phi_{13}]$ , a series of compounds exists with oIB vierer-single layers  $\frac{2}{z}[\text{B}_2\text{P}_3\Phi_{13}]$  which comprise isotypic or at least closely related structural arrangements. All borophosphates were synthesized hydrothermally and contain protonated anionic partial structures. A remarkable feature in this branch of borophosphates is the number of templated compounds obtained by using organic cations (amines) as structure directing agents.

**Borophosphates based on  $5\Box:\langle 3\Box\rangle=\langle 3\Box\rangle\Box$ .** The fundamental building unit  $5\Box:\langle 3\Box\rangle=\langle 3\Box\rangle\Box$  comprises only one unshared oxygen atom at one of the borate tetrahedra. Via this vertex the pentamer can be condensed forming loop-branched single chains  $\frac{1}{z}\{[\text{B}_2\text{P}_3\Phi_{13}]_m\}$  which are found protonated and unprotonated with different periodicities in the crystal structures of several known borophosphates (Table 7). A remarkable number of compounds contains organic cations and comprises isotypic or at least topologically equivalent structural arrangements of the complex anions. Most of the compounds in this branch of hierarchy were obtained by hydrothermal techniques. In case of  $\text{Rb}_3[\text{B}_2\text{P}_3\text{O}_{11}(\text{OH})_2]$  a solvothermal route with ethanol has been reported,  $\text{Na}_5[\text{B}_2\text{P}_3\text{O}_{13}]$  is obtained by various different methods of preparation.

### B:P = 1:2

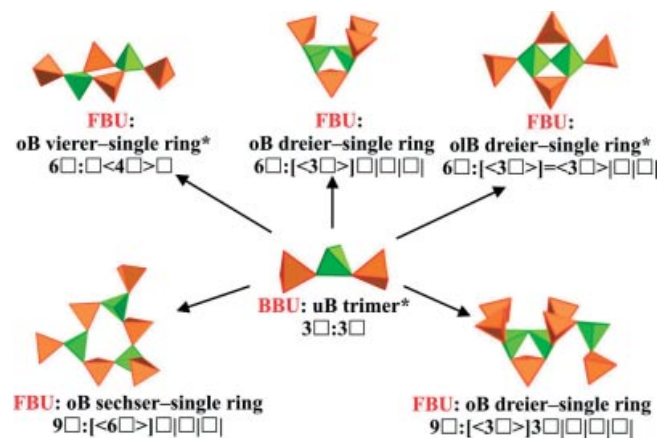
The largest group of tetrahedral borophosphates possesses a molar composition B:P = 1:2 comprising a large variety of complex anions ranging from simple oligomers to layers (a framework is only present in a series of beryllorborophosphates  $\text{M}^{\text{II}}[\text{BeBP}_2\text{O}_8]$  which is presented in section 4.3 “Metalborophosphates”). The simplest building unit consists of two phosphate groups connected to a borate tetrahedron (Fig. 12, BBU: uB trimer  $3\Box:3\Box$ ). By condensation of two or three of the BBUs a set of five fundamental building units (FBUs, Fig. 12) can be generated which contain the essential structural patterns of these compounds. Every FBU represents a starting point of a new branch, except

**Fig. 11** Condensation of mixed-branched (oIB) cyclic FBUs  $5\Box:\langle 3\Box\rangle=\langle 3\Box\rangle\Box$  forming loop-branched chains. These chains exist with different conformation, thus, different periodicities  $P$  are found („dreier“, „sechser“).**Table 7** Borophosphates with tetrahedral anions (B:P = 2:3) built from the oIB cyclic FBU  $5\Box:\langle 3\Box\rangle=\langle 3\Box\rangle\Box$ .

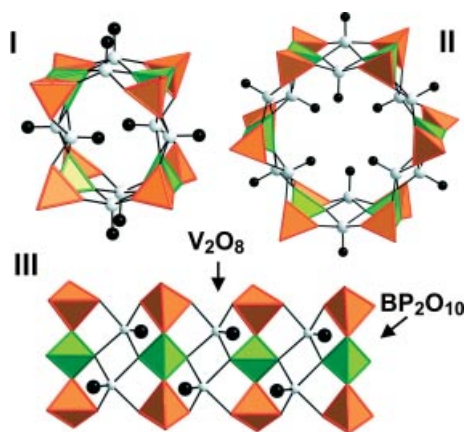
IB chains $\frac{1}{z}\{[\text{B}_2\text{P}_3\Phi_{13}]_m\}$ ( $\Phi = \text{O}, \text{OH}; m = 1, 2$ ) $D = 1; M = 1; Q^{n/CN}; \text{B}^{4/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
1:0	$\text{Na}_5[\text{B}_2\text{P}_3\text{O}_{13}]$ (dreier)	<i>P2_1</i> (No. 4)	S, H	[39]
12:1	$\text{Mn}(\text{C}_3\text{H}_{12}\text{N}_2)[\text{B}_2\text{P}_3\text{O}_{12}(\text{OH})]^{*\text{a}}$ $\text{M}^{\text{II}}(\text{C}_4\text{H}_{12}\text{N}_2)[\text{B}_2\text{P}_3\text{O}_{12}(\text{OH})]^{*\text{a}}$ $(\text{M}^{\text{II}} = \text{Mn}, \text{Co}, \text{Zn})$ (sechser) $\text{Mn}(\text{C}_6\text{H}_{14}\text{N}_2)_{0.5}(\text{C}_4\text{H}_{12}\text{N}_2)_{0.5}$ $[\text{B}_2\text{P}_3\text{O}_{12}(\text{OH})]^{*\text{a}}$	<i>Pmc2_1</i> (No. 26) <i>Ima2</i> (No.46) <i>Ima2</i> (No.46)	H H H	[40] [40–42] [40]
11:2	$\text{Rb}_3[\text{B}_2\text{P}_3\text{O}_{11}(\text{OH})_2]$ (dreier)	<i>P2_1/c</i> (No.14)	ST	[43]

<sup>a)</sup> The structural arrangements of these templated borophosphates are identical in terms of topology.

of the oIB dreier-single ring  $6\Box:\langle 3\Box\rangle=\langle 3\Box\rangle\Box\Box$  which cannot be further condensed due to the avoidance of P–O–P bonds. Those FBUs which exist as isolated anions (oligomers) are marked with an asterisk.

**Fig. 12** In the first hierarchy level of tetrahedral borophosphates with B:P = 1:2 five different FBUs are observed so far; formed by condensation of two or three BBUs  $3\Box:3\Box$ .





**Fig. 13** Borophosphate trimers  $[\text{BP}_2\Phi_{10}]$  ( $\Phi = \text{O}, \text{OH}$ ) together with  $\text{V}_2\text{O}_8$  units (dimers of square-pyramids) form cyclic clusters or ribbons (Compounds listed in Table 8).

**Borophosphates based on  $3\Box:3\Box$ .** In the simplest cases of tetrahedral borophosphates with B:P = 1:2, the FBU  $3\Box:3\Box$  is incorporated as isolated species. This group of borophosphates contains a great number of compounds forming V(IV)-heteropolyoxoanions. The borophosphate

trimers are interconnected by  $\text{V}_2\text{O}_8$  units (dimers of square-pyramids) forming cyclic clusters  ${}^9_z[(\text{VO})_2\text{BP}_2\text{O}_{10}^{3-}]_m$  ( $m = 4, 5, 6$ ) or ribbons. In Figure 13 heteropolyoxo-clusters built of four (I) and six units (II) are shown as well as a ribbon (III).

In the crystal structures containing the larger clusters ( $m = 6$ ) some of the cations (alkaline metal or ammonium) are located inside the anions (guests, indicated by  $\supset$  in the formula). Some of the heteropolyoxo-clusters are even stable in solution. Thus, in addition to hydrothermal techniques, diffusion and recrystallization experiments are applied in order to obtain new crystalline phases. The only tungsten borophosphate,  $\text{K}_5\{\text{W}_4\text{O}_{10}[\text{BP}_2\text{O}_8(\text{OH})_2][\text{HPO}_4]_2\} \cdot 0.5\text{H}_2\text{O}$  (in the original work misleadingly labeled as  $\text{K}_5[\text{W}_4\text{O}_8(\text{H}_2\text{BO}_4)(\text{HPO}_4)_2(\text{PO}_4)_2] \cdot 0.5\text{H}_2\text{O}$  [44]), likewise contains unbranched borophosphate trimers (and additional monohydrogenphosphate tetrahedra).

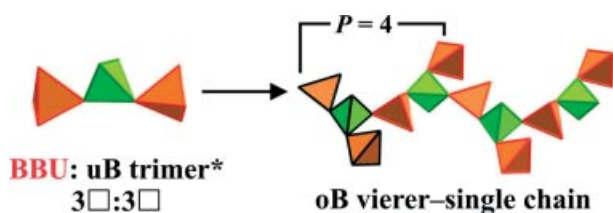
The unbranched BBU  $3\Box:3\Box$  can formally be condensed (avoiding oxygen-bridges between phosphate tetrahedra) to form open-branched single chains as shown in Figure 14. These chains are found with a periodicity  $P = 4$  in a series of isotypic borophosphates with the general chemical formula  $A\text{M}^{\text{III}}[\text{BP}_2\text{O}_8(\text{OH})]$  ( $A = \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$ ;  $\text{M}^{\text{III}} =$

**Table 8** Borophosphates which either contain unbranched borophosphate trimers  $[\text{BP}_2\text{F}_{10}]$  (BBU) or comprise anions which hierarchically originate from these.

O:OH	Compound	Oligomers $[\text{BP}_2\Phi_{10}]$ ( $\Phi = \text{O}, \text{OH}$ )		Synth.	Ref.
		$D = 0(t); M = 1; Q^{n/\text{CN}}; \text{B}^{2/4}, \text{P}^{1/4}$	SG		
1:0	$(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_3)_8[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 15\text{H}_2\text{O}$		<i>Pn</i> (No.7)	E	[45]
	$\text{TA}_4\text{H}[\text{M}(\text{VO})_{12}\{\text{BP}_2\text{O}_{10}\}_6] \cdot z\text{H}_2\text{O}$ ( $M = \text{NH}_4^+, \text{K}^+; z = 14, 16$ )		<i>Pbca</i> (No.61)	H, O	[46]
	$(\text{NH}_4)_x(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_y[(\text{NH}_4)\supset\text{V}_2\text{P}_2\text{BO}_{12}]_6$ ( $n = 7-18$ )		n.a.	E	[47]
	$(\text{C}_4\text{H}_{12}\text{N}_2)_6[(\text{VO})_2\text{BP}_2\text{O}_{10}]_4 \cdot z\text{H}_2\text{O}$ ( $z = 2, 14$ )			H	[48]
	$(z = 6)$		<i>P2_1/c</i> (No. 14)		
	$\text{Na}_{14}[\text{Na}\supset\{(\text{VO})_2\text{BP}_2\text{O}_{10}\}_5] \cdot n\text{H}_2\text{O}$		<i>P2_1/n</i> (No. 14)	H	[48]
	$\text{A}_1[\text{A}\supset\{(\text{VO})_2\text{BP}_2\text{O}_{10}\}_6] \cdot n\text{H}_2\text{O}$ ( $A = \text{NH}_4^+, \text{K}^+ - \text{Cs}^+$ )		<i>R3m</i> (No. 166) ( $A = \text{NH}_4$ )	H	[48]
	$[\text{C}_2\text{H}_{10}\text{N}_2]_2[(\text{VO})_5(\text{H}_2\text{O})\{\text{BP}_2\text{O}_{10}\}_2] \cdot 1.5\text{H}_2\text{O}$		<i>Fdd2</i> (No. 42)	H	[49]
	$(\text{NH}_4)_2(\text{C}_2\text{H}_{10}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{BP}_2\text{O}_{12}]_6 \cdot 10\text{H}_2\text{O}$		<i>C2/c</i> (No.15)	E	[50]
	$(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_4[\text{Sr}(\text{H}_2\text{O})_4]_2[\text{V}_2\text{BP}_2\text{O}_{12}]_6 \cdot 17\text{H}_2\text{O}$		<i>I2/m</i> (No.12)	E	[50]
4:1	$(\text{NH}_4)_3(\text{C}_4\text{H}_{14}\text{N}_2)_4[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{Sr}(\text{H}_2\text{O})_4][\text{V}_2\text{BP}_2\text{O}_{12}]_6 \cdot 10\text{H}_2\text{O}$		<i>C2/c</i> (No.15)	E	[50]
	$(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{Na}(\text{VO})_{10}\{\text{BP}_2\text{O}_8(\text{OH})_2\}_5] \cdot 22.5\text{H}_2\text{O}$		<i>P2_1/c</i> (No.14)	H	[51]
	$\text{CsV}_3(\text{H}_2\text{O})_2[\text{B}_2\text{P}_4\text{O}_{16}(\text{OH})_4]$		<i>C2/m</i> (No. 12)	H	[52]
	$\text{LiCu}_2[\text{BP}_2\text{O}_8(\text{OH})_2]$		<i>C2/c</i> (No. 15)	H	[53]
	$(\text{C}_3\text{H}_{12}\text{N}_2)\text{Fe}^{\text{III}}_6[\text{B}_4\text{P}_8\text{O}_{32}(\text{OH})_8]$		<i>P2_1/c</i> (No.14)	H	[54]
	$\text{K}_5\{\text{W}_4\text{O}_{10}[\text{BP}_2\text{O}_8(\text{OH})_2][\text{HPO}_4]_2\} \cdot 0.5\text{H}_2\text{O}^{\text{a}}$		<i>C2/c</i> (No. 15)	H	[44]
7:3	$\text{Mg}_2[\text{BP}_2\text{O}_7(\text{OH})_3]$		<i>P1</i> (No. 1)	H	[55]
	$A\text{M}^{\text{III}}[\text{BP}_2\text{O}_7(\text{OH})_3]$ ( $A = \text{Na}, \text{K}; \text{M}^{\text{III}} = \text{Al}, \text{V}, \text{Fe}, \text{Ga}, \text{In}$ )		<i>C2/c</i> (No. 15)	H	[56–61]
	$\text{CaNi}[\text{BP}_2\text{O}_7(\text{OH})_3]$		<i>C2/c</i> (No. 15)	H	[62]
<b>Chains <math>{}^1_z\{[\text{BP}_2\Phi_9]\}_m</math> (<math>\Phi = \text{O}, \text{OH}</math>) (<math>m = 2</math>)</b>					
$D = 1; M = 1; Q^{n/\text{CN}}; \text{B}^{3/4}, \text{P}^{1/4}, \text{P}^{2/4}$					
O:OH	Compound	SG		Synth.	Ref.
8:1	$A\text{M}^{\text{III}}[\text{BP}_2\text{O}_8(\text{OH})]$ $A = \text{NH}_4^+, \text{Rb}, \text{Cs}$ $\text{M}^{\text{III}} = \text{V}, \text{Fe}, (\text{Fe}_{0.53}\text{V}_{0.47}), \text{Al}, \text{Ga}$	<i>P2_1/c</i> (No. 14)		H	[63–73]
	$\text{Pb}_2[\text{BP}_2\text{O}_8(\text{OH})]$	<i>P2_1/n</i> (No. 14)		H	[74]

<sup>a</sup>) Additional isolated phosphate species are present besides the borophosphate anions. These are not regarded in the ratio B:P = 1:2.

Al, Ga, Fe, V) and in a lead compound  $\text{Pb}_2[\text{BP}_2\text{O}_8(\text{OH})]$ , all exclusively synthesized hydrothermally. A summary of all compounds known so far containing anionic partial structures based on unbranched trimers  $[\text{BP}_2\Phi_{10}]$  ( $\Phi = \text{O}, \text{OH}$ ) is given in Table 8.



**Fig. 14** Avoiding P–O–P-bonds, the unbranched BBU  $3\Box:3\Box$  can be condensed to form open-branched chains as present in a series of isotypic borophosphates  $AM^{\text{III}}[\text{BP}_2\text{O}_8(\text{OH})]$  ( $A = \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$ ;  $M^{\text{III}} = \text{Al}, \text{Ga}, \text{Fe}, \text{V}$ ) and  $\text{Pb}_2[\text{BP}_2\text{O}_8(\text{OH})]$  (see Table 8).

**Borophosphates based on  $6\Box:\Box<4\Box>\Box$ .** As already shown in the overview in Figure 12, two BBUs  $3\Box:3\Box$  may be condensed to form open-branched four-membered ring FBUs  $6\Box:\Box<4\Box>\Box$  in the first level of hierarchy. The isotypic compounds  $AM^{\text{III}}[\text{BP}_2\text{O}_8(\text{OH})]$  ( $A = \text{K}, \text{Rb}$ ;  $M^{\text{III}} = \text{Fe}, \text{In}$ ) comprise isolated and partially protonated oligomers  ${}^0[\text{B}_2\text{P}_4\text{O}_{16}(\text{OH})_2]$  and, thus, represent the simplest examples in this branch of borophosphates.

Chains with different periodicities can formally be disassembled into the hexameric FBU (Fig. 15). A remarkable number of chiral compounds crystallize with 1B zwölf-single chains  ${}^1_2[\text{BP}_2\text{O}_8^{3-}]$  which are wound around a left- or right-handed sixfold screw-axis ( $6_1$  or  $6_5$  helix) and which show a great flexibility in form when crystallizing with various cations or combinations of cations, respectively. The chiral architecture is closely related to the CZP-topology (chiral zincophosphate  $\text{Na}[\text{ZnPO}_4]\cdot\text{H}_2\text{O}$  [75]) and is also found in some zincoborophosphates (see section 4.3, metalborophosphates).

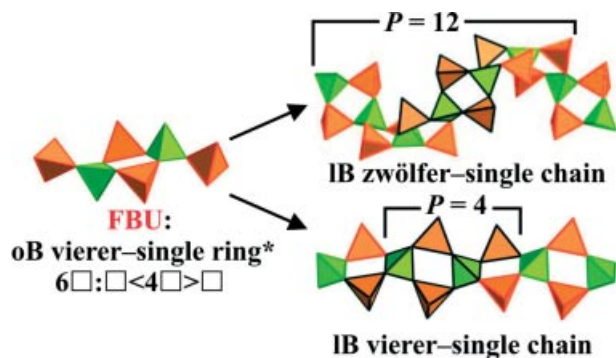
**Table 9** Borophosphate oligomers and chains hierarchically based on the open-branched cyclic FBU  $6\Box:\Box<4\Box>\Box$ .

O:OH	Compound	Oligomers ${}^0[\text{B}_2\text{P}_4\Phi_{18}]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 0(r); M = 1; Q^{i/CN}; B^{4/4}, P^{1/4}, P^{2/4}$		Synth.	Ref.	
		SG				
8:1	$AM^{\text{III}}[\text{BP}_2\text{O}_8(\text{OH})]$ ( $A = \text{NH}_4, \text{K}, \text{Rb}$ ; $M^{\text{III}} = \text{Sc}, \text{Fe}, \text{In}$ )	$P\bar{1}$ (No. 2)		H	[58, 76–80]	
	$\text{Pb}M^{\text{II}}[\text{BP}_2\text{O}_8(\text{OH})]$ $M^{\text{II}} = \text{Co}, \text{Zn}$	$P\bar{1}$ (No. 2)		H	[81]	
Chains ${}^1_2[(\text{B}_2\text{P}_4\Phi_{16})_m]$ ( $\Phi = \text{O}, \text{OH}$ ) ( $m = 1, 3$ ) <sup>a)</sup> $D = 1; M = 1; Q^{i/CN}; B^{4/4}, P^{2/4}$						
O:OH	Compound	SG		Synth.	Ref.	
1:0	$M^{\text{III}}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ ( $M^{\text{III}} = \text{Sc}, \text{Fe}, \text{In}$ )	$P6_122$ (No. 178)/ $P6_522$ (No. 179)		H	[82–84]	
	$M^{\text{III}}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]$ ( $M^{\text{III}} = \text{Sc}, \text{In}$ )	$P6_122$ (No. 178)/ $P6_522$ (No. 179)		S <sup>a)</sup>	[82, 85, 86]	
	$\text{In}[\text{BP}_2\text{O}_8]\cdot 0.8\text{H}_2\text{O}^{\text{b)}$	$P6_122$ (No. 178)		H	[87]	
	$AM^{\text{II}}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ ( $A = \text{NH}_4, \text{Li-K}, M^{\text{II}} = \text{Mg}, \text{Mn-Zn}$ )	$P6_1$ (No. 169)/ $P6_5$ (No. 170)		H	[88–96]	
	$(\text{H}_3\text{O})\text{Zn}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$	$P6_122$ (No. 178)/ $P6_522$ (No. 179)		H	[97]	
	$\text{NaCd}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.8\text{H}_2\text{O}$	$P6_122$ (No. 178)		H	[98]	
	$(\text{NH}_4)\text{Cd}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.72\text{H}_2\text{O}$	$P6_5$ (No. 170)		H	[99]	
	$\text{KFe}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.5\text{H}_2\text{O}$	$P6_122$ (No. 178)		H	[95]	
	$A_xM_y(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot z\text{H}_2\text{O}^{\text{c)}$ ( $A = \text{Rb}, \text{Cs}, M = \text{Mg}, \text{Mn}, \text{Co}, \text{Fe}^{\text{II/III}}$ )	$P6_122$ (No. 178)/ $P6_522$ (No. 179)		H	[100]	
	$(\text{H}_3\text{O})_{0.5}M^{\text{II}}_{1.25}(\text{H}_2\text{O})[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ ( $M^{\text{II}} = \text{Co}, \text{Mn}$ )	$P6_122$ (No. 178)		H	[101]	
	$(\text{NH}_4)_{0.4}\text{Fe}^{\text{II}}_{0.55}\text{Fe}^{\text{III}}_{0.5}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.6\text{H}_2\text{O}$	$P6_5$ (No. 170)/ $P6_522$ (No. 179)		H	[64]	
	$(\text{NH}_4)_{0.5}\text{Fe}^{\text{II}}_{0.5}\text{Fe}^{\text{III}}_{0.5}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot 0.5\text{H}_2\text{O}$	$P6_5$ (No. 170)		H	[102]	
	$\{(\text{NH}_4)_x\text{Co}_{(3-x)/2}\}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot z\text{H}_2\text{O}$ ( $x \approx 0.5$ )	$P6_5$ (No. 170)		H	[103]	
	$\text{Ca}_{0.5}\text{Ni}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}^{\text{c)}$	$P6_122$ (No. 178)		H	[104]	
	$(\text{Mg}_{1-x}M^{\text{II}}_x)(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot z\text{H}_2\text{O}^{\text{c)}$ ( $M^{\text{II}} = \text{Mg-Ba}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}$ )	$P6_122$ (No. 178)/ $P6_522$ (No. 179)		H	[86]	
	1:0	$\text{Na}_3[\text{BP}_2\text{O}_8]$	$C2/c$ (No. 15)		F	[105]
	7:1	$(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{B}_2\text{P}_4\text{O}_{14}(\text{OH})_2]$	$P2_1/n$ (No. 14)		H	[106]

<sup>a)</sup> All helical borophosphates contain zwölf-single chains ( $m = 3$ ). In the crystal structures of  $\text{Na}_3[\text{BP}_2\text{O}_8]$  and  $(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{B}_2\text{P}_4\text{O}_{14}(\text{OH})_2]$  the chains comprise the periodicity  $P = 4$  ( $m = 1$ ).

<sup>b)</sup> Most probably identical with  $\text{In}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ ; misleadingly reported to contain  $\text{InO}_4$  tetrahedra.

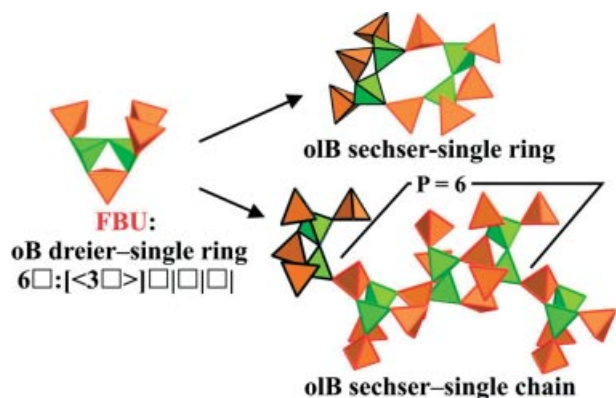
<sup>c)</sup> Additional reflections in the X-ray diffraction patterns point to possible super-structures or twinning. When refined in the sub-cell the structures show partially disordered cations.



**Fig. 15** Condensation of the open-branched vierer-single ring forming loop-branched chains with different periodicities (conformations). All known borophosphates based on this hexameric FBU are summarized in Table 9.

The borophosphates with partial structures based on  $6\Box:\Box<4\Box>\Box$  are summarized in Table 9, and are usually obtained by hydrothermal syntheses. The two unshared oxygen corners, one at each of the two borate tetrahedra, furthermore allow the hexameric FBU to be connected to layers, but these patterns have hitherto only been observed in a metalloborophosphate (see section 4.3; Metalloborophosphates).

**Borophosphates based on  $6\Box:\Box<3\Box>\Box\Box\Box$ .** Two BBUs  $3\Box:3\Box$  may be condensed via two common oxygen atoms forming an open-branched dreier-single ring (Fig. 16, left). This FBU only comprises one unshared borate oxygen atom. Thus, only linear condensation is possible and the dimensionality of the anions formed is limited due to the avoidance of oxygen-bridges between phosphate tetrahedra. Hitherto only two different partial structures have been observed: a mixed-branched(oIB) sechser-single ring and a mixed-branched(oIB) sechser-single chain as shown in Figure 16. The corresponding borophosphates, both obtained by hydrothermal synthesis, are listed in Table 10.



**Fig. 16** Mixed branched(oIB) sechser-single ring and mixed branched(oIB) sechser-single chain built from the FBU  $6\Box:\Box<3\Box>\Box\Box\Box$ . The presence of only one unshared oxygen atom at one of the borate tetrahedra limits the dimensionality of the borophosphate partial structures when the FBUs are interconnected. For corresponding borophosphates see Table 10.

**Table 10** Tetrahedral borophosphates hierarchically based on the FBU  $6\Box:\Box<3\Box>\Box\Box\Box$ .

Oligomers $\{[B_2P_4\Phi_{17}]_2\}$ ( $\Phi = O, OH$ ) $D = 0(r); M = 1; Q^{n/CN}: B^{4/4}, P^{1/4}, P^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
14:3	$K_6Cu_2[B_4P_8O_{28}(OH)_6]$	$P2_1/c$ (No. 14)	H	[107]
Chains $\frac{1}{2}\{[B_2P_4\Phi_{17}]_m\}$ ( $\Phi = O, OH$ ) ( $m = 3$ ) $D = 1; M = 1; Q^{n/CN}: B^{4/4}, P^{3/4}$				
O:OH	Compound	SG	Synth.	Ref.
39:12	$Zn_3(C_6H_{14}N_2)_4[B_6P_{12}O_{39}(OH)_{12}][HPO_4]^{3-}$	$R3$ (No.146)	H	[108]

<sup>a)</sup> The crystal structure contains additional hydrogenphosphate groups besides the borophosphate anions. Counting in these additional units leads to a ratio B:P = 6:13.

**Borophosphates based on  $6\Box:\Box<3\Box>=\Box<3\Box>\Box\Box\Box$ .** If two of the BBUs  $3\Box:3\Box$  are condensed sharing three oxygen atoms in the way that a mixed branched (oIB) dreier-single ring is formed like shown in Figure 17, all oxygen atoms of the borate tetrahedra are shared with adjacent tetrahedra ( $B^{4/4}$ ). Due to the terminal character of the  $PO_4$ -groups the FBU can not be interlinked to form anionic partial structures of higher dimensionality. Only one borophosphate containing isolated anions of the type  $6\Box:\Box<3\Box>=\Box<3\Box>\Box\Box\Box$  has been reported so far:  $Na_4Cu_3[B_2P_4O_{15}(OH)_2]\cdot 2HPO_4$  (see Table 11). Just one anion-substituted zincborophosphate is known to contain this type of anions as well (see section 4.3, "Metalloborophosphates").  $Na_4Cu_3[B_2P_4O_{15}(OH)_2]\cdot 2HPO_4$  has been synthesized hydrothermally and contains isolated  $[HPO_4^{2-}]$  anions besides the borophosphate partial structure.



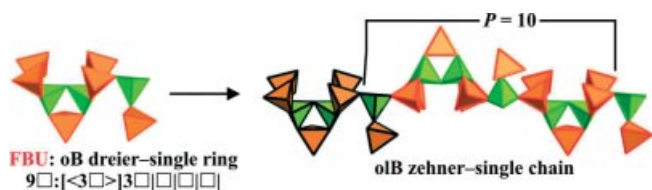
**Fig. 17** The FBU  $6\Box:\Box<3\Box>=\Box<3\Box>\Box\Box\Box$  contains only borate tetrahedra with a connectedness  $Q^{n/CN} = B^{4/4}$  and can not further be condensed due to the terminal character of the phosphate groups.

**Table 11** Borophosphates containing oIB dreier-single rings  $6\Box:\Box<3\Box>\Box\Box\Box$ .

Oligomers $\frac{1}{2}[B_2P_4\Phi_{17}]$ ( $\Phi = O, OH$ ) $D = 0(r); Q^{n/CN}: B^{4/4}, P^{1/4}, P^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
15:2	$Na_4Cu_3[B_2P_4O_{15}(OH)_2]\cdot 2HPO_4$	$C2/c$ (No. 15)	H	[109]

<sup>a)</sup> The crystal structure contains additional hydrogenphosphate groups besides the borophosphate oligomers. Counting in these additional units leads to a ratio B:P = 1:3.

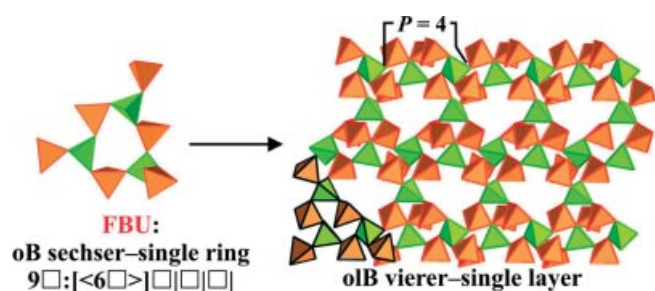
**Borophosphates based on  $9\text{O}:[<3\text{O}>]3\text{O}[\text{O}]\text{O}[\text{O}]$ .** The nonameric FBU is built from three unbranched BBUs  $3\text{O}:[<3\text{O}>]$  which are connected in different ways. Two trimers share two common oxygen atoms forming an open-branched ring ( $6\text{O}:[<3\text{O}>]2\text{O}[\text{O}]\text{O}[\text{O}]$ , see Fig. 16), the third trimer is found as a branch attached to the three-membered ring (Fig. 18, left). With a  $\text{B}^{2/4}$  tetrahedron the nonameric FBUs can be condensed to borophosphates of higher dimensionality. Hitherto only mixed-branched (olB) single chains with a periodicity  $P = 10$  (Fig. 18, right) have been observed in a templated iron borophosphate which was obtained by hydrothermal synthesis (Table 12).



**Fig. 18** Linear condensation of nonameric FBUs  $9\text{O}:[<3\text{O}>]3\text{O}[\text{O}]\text{O}[\text{O}]$  forming a mixed-branched (olB) zehner-einfach chain like present in the crystal structure of  $(\text{C}_4\text{H}_{10}\text{N}_2)_3\text{Fe}_6(\text{H}_2\text{O})_4[\text{B}_6\text{P}_{12}\text{O}_{42}(\text{OH})_{12}]$  (see Table 12).

**Table 12** Borophosphates based on the FBU  $9\text{O}:[<3\text{O}>]3\text{O}[\text{O}]\text{O}[\text{O}]$  (olB dreier-single ring).

Chains $\frac{1}{2}\{\text{B}_3\text{P}_{16}\Phi_{27}\}_m$ ( $\Phi = \text{O}, \text{OH}$ ) ( $m = 2$ )				
$D = 1; Q^{olCN}: \text{B}^{3/4}, \text{B}^{4/4}, \text{P}^{1/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
7:2	$(\text{C}_4\text{H}_{10}\text{N}_2)_3\text{Fe}_6(\text{H}_2\text{O})_4[\text{B}_6\text{P}_{12}\text{O}_{42}(\text{OH})_{12}]$	<i>Pbca</i> (No. 61)	H	[110]



**Fig. 19** Formation of olB vierer-single layers by condensation of nonameric FBUs  $9\text{O}:[<6\text{O}>]2\text{O}[\text{O}]\text{O}[\text{O}]$ .

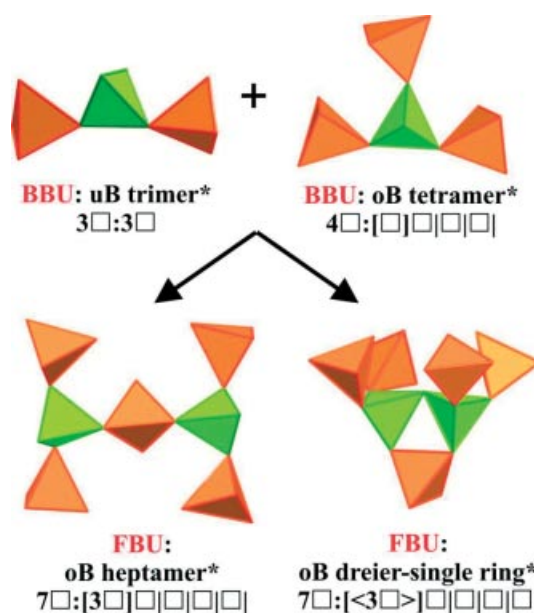
**Table 13** Tetrahedral borophosphates with anionic partial structures referred to the FBU  $9\text{O}:[<6\text{O}>]2\text{O}[\text{O}]\text{O}[\text{O}]$ .

Layers $\frac{2}{3}\{\text{B}_3\text{P}_6\Phi_{24}\}_m$ ( $\Phi = \text{O}, \text{OH}$ ) ( $m = 1$ )				
$D = 2; M = 1; Q^{olCN}: \text{B}^{4/4}, \text{P}^{1/4}, \text{P}^{2/4}, \text{P}^{3/4}$				
O:OH	Compound	SG	Synth.	Ref.
7:1	$M^I_2[\text{BP}_2\text{O}_7(\text{OH})]$ $M^I = \text{Na}, (\text{Na}_{1.89}\text{Ag}_{0.11})$	<i>Pna2</i> <sub>1</sub> (No.33)	H	[111]

**Borophosphates based on  $9\text{O}:[<6\text{O}>]2\text{O}[\text{O}]\text{O}[\text{O}]$ .** By interconnection of three BBUs  $3\text{O}:[<3\text{O}>]$  avoiding contacts between phosphate tetrahedra, an open-branched six-membered single ring of the type  $9\text{O}:[<6\text{O}>]2\text{O}[\text{O}]\text{O}[\text{O}]$  is formed (Fig. 19, left). The nonamer comprises unshared oxygen atoms at each borate tetrahedron which allow the FBU to form anions of higher dimensionality. Up to date only mixed branched (olB) vierer-single layers (Fig. 19, right) are known in this branch of compounds, observed in the crystal structures of two isotopic borophosphates  $M^I_2[\text{BP}_2\text{O}_7(\text{OH})]$  ( $M^I = \text{Na}, \text{Na}_{1.89}\text{Ag}_{0.11}$ ) which were both synthesized hydrothermally (see Table 13).

### B:P = 2:5

Up to date the number of tetrahedral borophosphates with a molar ratio of B:P = 2:5 is small. The FBUs in this branch of compounds are formed by formally condensing the BBUs with B:P = 1:2 (uB trimer) and B:P = 1:3 (oB trimer). As shown in Fig. 20, an open-branched heptamer ( $7\text{O}:[3\text{O}]\text{O}[\text{O}]\text{O}[\text{O}]\text{O}[\text{O}]$ ) and an open-branched dreier-single ring ( $7\text{O}:[<3\text{O}>]2\text{O}[\text{O}]\text{O}[\text{O}]\text{O}[\text{O}]$ ) have been observed, with the BBUs interconnected via one and two common oxygen vertices, respectively.



**Fig. 20** FBUs of tetrahedral borophosphates with B:P = 2:5: An open-branched heptamer and an open-branched dreier-single ring are formed by condensation of the BBUs with B:P = 1:2 and B:P = 1:3. Borophosphates originating from these FBUs are summarized in Tables 14 and 15, respectively.

**Table 14** Tetrahedral borophosphates (B:P = 2:5) built from oB heptameric FBUs  $7\text{O}:[3\text{O}]\text{O}[\text{O}]\text{O}[\text{O}]\text{O}[\text{O}]$ .

Oligomers $[\text{B}_2\text{P}_5\Phi_{22}]$ ( $\Phi = \text{O}, \text{OH}$ )				
$D = 0(t); M = 1; Q^{olCN}: \text{B}^{3/4}, \text{P}^{1/4}, \text{P}^{2/4}$				
O:OH	Compound	SG	Synth.	Ref.
1:0	$(\text{N}_2\text{C}_3\text{H}_5)_{3.8}(\text{H}_3\text{O})_{1.2}[(\text{VO})_4\text{B}_2\text{P}_5\text{O}_{22}] \cdot 0.3\text{H}_2\text{O}$	<i>C2/c</i> (No.15)	H	[112]

**Borophosphates based on  $7\text{□}:[3\text{□}]\text{□}\text{□}\text{□}\text{□}$ .** The oB heptamers (Fig. 20, bottom left) may form anions of higher dimensionality as  $\text{B}^{3/4}$  tetrahedra are present which allow further condensation. Nevertheless, in the only known borophosphate in this hierarchical branch,  $(\text{N}_2\text{C}_3\text{H}_5)_{3.8}(\text{H}_3\text{O})_{1.2}[(\text{VO})_4\text{B}_2\text{P}_5\text{O}_{22}] \cdot 0.3\text{H}_2\text{O}$ , the  $7\text{□}:[3\text{□}]\text{□}\text{□}\text{□}\text{□}$  units are present as “isolated” species. As part of layered heteropolyoxoanions  ${}_{\infty}^2[\text{V}^{\text{IV}}_4\text{B}_2\text{P}_5\text{O}_{26}]^{5-}$  the heptamers are interconnected via  $\text{VO}_5$  (square pyramid) and  $\text{V}_2\text{O}_8$  units (edge-sharing pyramids). The compound was obtained via hydrothermal synthesis and contains organic molecule cations (see Tab. 14).

**Borophosphates based on  $7\text{□}:[<3\text{□}>]\text{□}\text{□}\text{□}\text{□}$ .** The cyclic FBUs  $7\text{□}:[<3\text{□}>]\text{□}\text{□}\text{□}\text{□}$  (Fig. 20, bottom right) can not be interconnected due to the avoidance of P–O–P bonds. In the crystal structure of  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{VB}_2\text{P}_5\text{O}_{17}(\text{OH})_5] \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{PO}_4$  which has to be described as an adduct containing “free” phosphoric acid, the cyclic borophosphate partial structure is involved in a heteropolyoxoanion forming a  $[\text{V}^{\text{IV}}\text{OB}_2\text{P}_5\text{O}_{16}(\text{OH})_5]^{4-}$  cluster (A corresponding cluster is known with the mixed-coordinated anion  $\Delta 6\text{□}:[<\Delta 2\text{□}>]\text{□}\text{□}\text{□}\text{□}$  (B:P = 3:4, see Fig. 25 in section 4.2 “Mixed-coordinated borophosphates”). The borophosphate under consideration was obtained by hydrothermal synthesis and comprises templating organic molecule cations (Table 15).

**Table 15** Open-branched dreier-single rings as FBU of tetrahedral borophosphates with B:P = 2:5.

O:OH	Compound	SG	Synth.	Ref.
16:5	$(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{VOB}_2\text{P}_5\text{O}_{16}(\text{OH})_5] \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{PO}_4^{\text{a}}$	$P2_1/c$ (No.14)	H	[113]

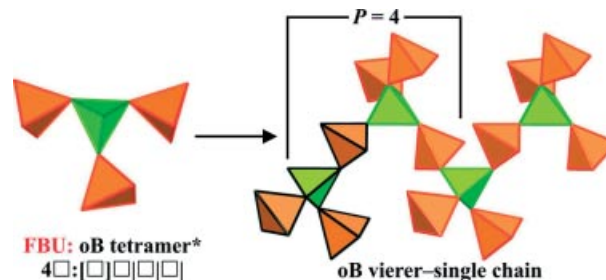
<sup>a)</sup> In crystal structure additional phosphate units are present besides the borophosphate anions. If these additional units are counted as well a ratio B:P = 1:3 results.

### B:P = 1:3

Due to the avoidance of P–O–P-bonds the variety of tetrahedral borophosphates with B:P = 1:3 is clearly limited. All compounds in this hierarchical branch are referred to a FBU (= BBU in this case) built of three phosphate tetrahedra attached to one central borate tetrahedron: an open branched tetramer ( $4\text{□}:[\text{□}]\text{□}\text{□}\text{□}$ ).

**Borophosphates based on  $4\text{□}:[\text{□}]\text{□}\text{□}\text{□}$ .** The tetrameric BBU  $4\text{□}:[\text{□}]\text{□}\text{□}\text{□}$  may either exist as isolated anion  $[\text{BP}_3\Phi_{13}]$  ( $\Phi = \text{O}, \text{OH}$ ) or as FBU of borophosphate partial structures with larger extension. As the borate tetrahedron comprises only one unshared oxygen atom, the dimensionality of the borophosphates formed is limited to  $D = 1$  (chains) due to the avoidance of P–O–P bonds. Although different oligomers, such as rings and chains may be created by interconnecting the tetramers only open-branched strands with a periodicity  $P = 4$  (vierer-single) have been

observed to date (Fig. 21). These comprise the highest possible phosphate content for chains without connections between phosphate tetrahedra.



**Fig. 21** Interconnection of open-branched tetramers (FBU) forming an open-branched vierer-single chain as observed (protonated and non-protonated) in borophosphates with B:P = 1:3 (Table 16).

The tetrahedral borophosphates with B:P = 1:3 known so far are listed in Table 16. Non-protonated oligomers  $[\text{BP}_3\Phi_{13}]$  ( $\Phi = \text{O}, \text{OH}$ ) are found connected to a  $\text{V}_3\text{O}_{13}$  triple of V(V) coordination octahedra (three octahedra sharing a central oxygen atom, interconnected via common edges) forming isolated clusters  ${}_{\infty}^0[\text{V}_3\text{BP}_3\text{O}_{19}]$ . Protonated open-branched tetramers are found as “free” anions in the crystal structures of  $(\text{NH}_4)_4\text{Mn}_9[\text{BP}_3\text{O}_{11}(\text{OH})_2]_2[\text{HPO}_4]_2\text{-}[\text{PO}_4]_2$  and  $\text{Mg}_2(\text{H}_2\text{O})[\text{BP}_3\text{O}_9(\text{OH})_4]$ . All compounds were obtained from aqueous media either hydrothermally (H) or by crystallization in an open system (O).  $\text{Mg}_2(\text{H}_2\text{O})\text{-}[\text{BP}_3\text{O}_9(\text{OH})_4]$  could as well be obtained solvothermally in ethanol.

**Table 16** Tetrahedral borophosphates with B:P = 1:3 hierarchically originating from open-branched tetramers  $4\text{□}:[\text{□}]\text{□}\text{□}\text{□}$ .

O:OH	Compound	SG	Synth.	Ref.
1:0	$(\text{NH}_4)_5[\text{V}_3\text{BP}_3\text{O}_{19}] \cdot \text{H}_2\text{O}$	$P\bar{1}$ (No.2)	O	[114]
	$[\text{Co}(\text{en})_3][\text{enH}_2][\text{V}_3\text{BP}_3\text{O}_{19}] \cdot 4.5\text{H}_2\text{O}$	$P2_1/c$ (No.14)	H	[115]
	$[\text{Co}(\text{en})_3]_2[\text{V}_3\text{BP}_3\text{O}_{19}][\text{H}_2\text{PO}_4] \cdot 4\text{H}_2\text{O}^{\text{a}}$	$C2/c$ (No. 15)	H	[116]
11:2	$(\text{NH}_4)_4\text{Mn}_9[\text{BP}_3\text{O}_{11}(\text{OH})_2]_2[\text{HPO}_4]_2\text{-}[\text{PO}_4]_2^{\text{b}}$	$C2/c$ (No. 15)	H	[117]
9:4	$\text{Mg}_2(\text{H}_2\text{O})[\text{BP}_3\text{O}_9(\text{OH})_4]$	$P2_12_12_1$ (No. 19)	H, ST	[32]

O:OH	Compound	SG	Synth.	Ref.
1:0	$M^{\text{II}}_3[\text{BP}_3\text{O}_{12}]$			
	$M^{\text{II}} = \text{Ba}$	$Ibca$ (No. 73)	S	[1]
	$M^{\text{II}} = \text{Pb}$	$Pbca$ (No. 61)	S	[118]
3:1	$\text{K}_3[\text{BP}_3\text{O}_9(\text{OH})_3]$	$C2/c$ (No. 15)	ST	[43]

<sup>a)</sup> Compound contains isolated hydrogenphosphate tetrahedra besides the borophosphate anions resulting in an overall ratio B:P = 1:4.

<sup>b)</sup> Isolated phosphate and hydrogenphosphate tetrahedra are present in the crystal structure. Counting in these additional phosphate units results in an overall B:P ratio of 1:5.

Regardless the presence of constitutional water (OH groups) in the case of  $\text{K}_3[\text{BP}_3\text{O}_9(\text{OH})_3]$ , the crystal structures of the compounds with open-branched vierer-single chains  ${}_{\infty}^1\{\text{BP}_3\Phi_{12}\}_m$  ( $\Phi = \text{O}, \text{OH}$ ) are structurally closely

related. Whereas the compounds  $M^{II}_3[BP_3O_{12}]$  were obtained by solid state reactions, the potassium borophosphate was synthesized solvothermally using ethanol as solvent.

### B:P = 1:4

With a B:P ratio of 1:4 the central borate tetrahedron is completely surrounded by phosphate groups (Fig. 22). No further connections to form anionic partial structures of higher dimensionalities are possible. A summary of all compounds comprising open-branched tetrameric anions  $5\Box:[\Box]\Box[\Box]\Box$  is given in Table 17.



**Fig. 22** Open-branched tetramers  $5\Box:[\Box]\Box[\Box]\Box$  can not be further interconnected due to the avoidance of P–O–P bonds and are, thus, only observed as isolated anions (Corresponding compounds listed in Table 17).

**Table 17** Tetrahedral borophosphates (B:P = 1:4) containing open-branched tetramers  $5\Box:[\Box]\Box[\Box]\Box$ .

O:OH Compound	Oligomers $^n[BP_4\Phi_{16}]$ ( $\Phi = O, OH$ ) $D = 0(t); M = 1; Q^{u/CN}: B^{u/4}, P^{1/4}$	SG	Synth. Ref.
1:0	$M^{II}_6[BP_4O_{16}][PO_4]^a$ $M^{II} = Pb$ $M^{II} = Sr$	$P\bar{4}$ (No. 81) $I4c2$ (No. 120)	H [119, 120] H, S [121]
16:3	$(C_3N_2H_5)_8[Mo_{12}B_2P_8O_{59}(OH)_3]\cdot 4H_2O$	$C2/c$ (No. 15)	H [122]

<sup>a)</sup> Compounds comprises additional phosphate groups besides the borophosphate oligomers (overall ratio B:P = 1:5).

The anions are non-protonated in compounds  $M^{II}_6[BP_4O_{16}][PO_4]$  ( $M^{II} = Pb, Sr$ ) which additionally contain isolated  $PO_4$  tetrahedra. The crystal structure of  $(C_3N_2H_5)_8[Mo_{12}B_2P_8O_{59}(OH)_3]\cdot 4H_2O$  contains heteropolyoxoclusters closely related to *Wells-Dawson*-clusters arranged around spacious organic molecule cations. In the clusters two protonated borophosphate pentamers cap a double ring of  $MoO_6$  coordination octahedra. A corresponding cluster is observed in a partially substituted compound containing phenylphosphonate groups (see section 4.4, “Anion-substituted compounds and border-cases”). The known compounds with B:P = 1:4 were synthesized either hydrothermally or by solid state reactions.

### 4.2 Mixed-coordinated borophosphates

Borophosphates with mixed-coordinated anions comprise a large variety in composition with B:P ratios ranging from

6:1 to 1:3. Nevertheless, the number of compounds known is comparatively small what hampers a detailed hierarchical classification. In contrast to tetrahedral borophosphates the anions of mixed coordinated borophosphates comprise a limited dimensionality: Hitherto only oligomers and chains have been observed. A general distinction is made between borate-rich compounds (B:P > 1:1) and phosphate rich compounds (B:P ≤ 1:1). This appears meaningful as the complexity of building units likewise differs with the composition. Whereas phosphate-rich compounds are built from rather simple building blocks, larger and more complex units are found with increasing borate content. Segments just containing borate groups occur which comprise connection patterns known from the structural chemistry of borates.

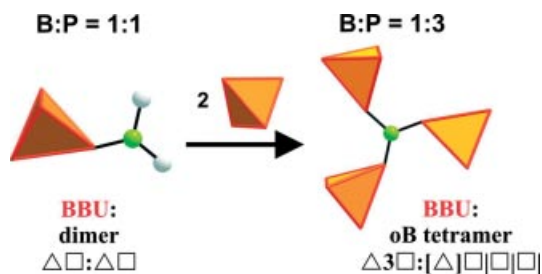
Common structural features of tetrahedral and mixed coordinated borophosphates are found in the general tendency to form three- and four-membered rings as well as in the appearance of open-branches and additional phosphate groups besides the borophosphate anions at low B:P ratios (avoidance of P–O–P bonds).

### B:P = 1:1 – 1:3

By focusing on mixed-coordinated partial structures with B:P ≤ 1:1 common features with tetrahedral borophosphates are easily recognized. As a trigonal planar borate unit can only be connected to three phosphate tetrahedra, the B:P ratio of mixed coordinated borophosphates is limited to a minimum of 1:3. A dimer  $\Delta\Box$  (Fig. 23, left) represents the simplest mixed-coordinated borophosphate building unit (B:P = 1:1). Isolated dimeric anions  $[BPO_6]$  are found in crystal structure of  $Co_5[BPO_6][PO_4]_2$  (B:P = 1:1) which additionally contains isolated phosphate tetrahedra (see Table 18). In correspondence with the BBU sequences of tetrahedral borophosphates (B:P = 1:1–1:4, see BBUs in Fig. 4) an open branched-tetramer  $\Delta 3\Box:[\Delta]\Box[\Box]\Box$  (B:P = 1:3) results by formal condensation of two further phosphate tetrahedra to the borate triangle (Fig. 23, right). These tetramers exist in a series of compounds  $M^{II-1}_2[BP_3O_{12}]$  ( $M = Cr, V, Fe$ ) which are identical in terms of topology but may differ in symmetry (Table 18). Mixed-coordinated borophosphates with B:P = 1:2 have not been observed so far. All known phosphate-rich compounds with mixed-coordinated anions were obtained by solid state reactions and flux methods.

Up to date only two more mixed-coordinated partial structures with B:P ≤ 1:1 have been observed. With a B:P ratio of 2:3, the crystal structure of  $CsSc[B_2P_3O_{11}(OH)_3]$  (Table 19) comprises oB dreier-single rings  $\Delta 4\Box:\Box<\Delta 2\Box>\Box$  which, following the hierarchical system presented for tetrahedral borophosphates, can be formed by formal condensation of the BBUs  $\Delta\Box:\Delta\Box$  (B:P = 1:1) and the unbranched tetrahedral trimer  $3\Box:3\Box$  (B:P = 1:2) as shown in Figure 24.

The crystal structure of  $[C_6H_{14}N_2]_2[VOB_3P_4O_{15}(OH)_5]\cdot 4H_2O$  (Table 19) comprises open-



**Fig. 23** A dimer  $\Delta\Box:\Delta\Box$  (B:P = 1:1) represents the simplest anion of mixed-coordinated borophosphates (left). Open-branched tetramers  $\Delta 3\Box:[\Delta]\Box\Box\Box$  have the highest possible phosphate content of mixed-coordinated borophosphates. The building unit results from formally attaching two further phosphate tetrahedra to the borate triangle. Both BBU have been observed as isolated anions in borophosphates (Table 18).

**Table 18** Mixed coordinated borophosphates with B:P = 1:1 and B:P = 1:3 comprising simple oligomeric anions (dimers  $\Delta\Box:\Delta\Box$ , open-branched tetramers  $\Delta 3\Box:[\Delta]\Box\Box\Box$ ).

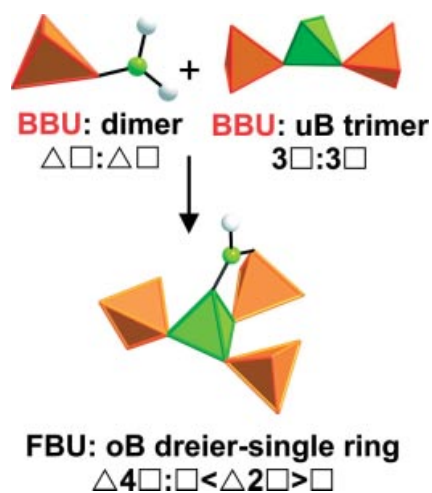
B:P = 1:1		Oligomers $[\text{BP}\Phi_7]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 0(t); M = 1; Q^{n/CN}: \text{B}^{1/3}, \text{P}^{1/4}$			
O:OH	Compound	SG	Synth.	Ref.	
1:0	$\text{Co}_5[\text{BPO}_6][\text{PO}_4]_2^{\text{a}}$	$P2_1/c$ (No. 14)	F	[123]	
B:P = 1:3		Oligomers $[\text{BP}_3\Phi_{12}]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 0; M = 1; Q^{n/CN}: \text{B}^{3/3}, \text{P}^{1/4}$			
O:OH	Compound	SG	Synth.	Ref.	
1:0	$M^{\text{III}}_2[\text{BP}_3\text{O}_{12}]$	$P3$ (No. 143)	S	[124, 125]	
	$M^{\text{III}} = \text{Cr}, \text{Fe}$	$P6_3/m$ (No. 176)	S	[126]	
	$M^{\text{III}} = \text{V}$				

<sup>a)</sup> Crystal structure comprises two isolated phosphate tetrahedra per formula unit (overall ratio B:P = 1:3).

**Table 19** Mixed-coordinated borophosphates with B:P = 2:3 and 3:4 comprise open branched three-membered ring anions.

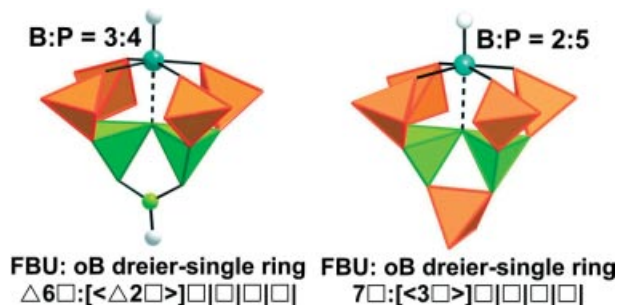
B:P = 2:3		Oligomers $[\text{B}_2\text{P}_3\Phi_{14}]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 0(r); M = 1; Q^{n/CN}: \text{B}^{2/3}, \text{B}^{4/4}, \text{P}^{1/4}, \text{P}^{2/4}$			
O:OH	Compound	SG	Synth.	Ref.	
11:3	$\text{CsSc}[\text{B}_2\text{P}_3\text{O}_{11}(\text{OH})_3]$	$Pbnm$ (No. 52)	H	[127]	
B:P = 3:4		Oligomers $[\text{B}_3\text{P}_4\Phi_{20}]$ ( $\Phi = \text{O}, \text{OH}$ ) $D = 0(r); M = 1; Q^{n/CN}: \text{B}^{2/3}, \text{B}^{4/4}, \text{P}^{1/4}$			
O:OH	Compound	SG	Synth.	Ref.	
3:1	$[\text{C}_6\text{H}_{14}\text{N}_2]_2[\text{VOB}_3\text{P}_4\text{O}_{15}(\text{OH})_3] \cdot 4\text{H}_2\text{O}$	$P2_1/c$ (No. 14)	H	[128]	

branched dreier-single rings  $\Delta 6\Box:[<\Delta 2\Box>]\Box\Box\Box\Box$  as part of a heteropolyoxocluster with vanadium (Fig. 25, left). A corresponding cluster containing a purely tetrahedral borophosphate  $7\Box:[<3\Box>]\Box\Box\Box\Box$  (B:P = 2:5, Fig. 25, right) is found in the crystal structure of  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{VOB}_2\text{P}_5\text{O}_{16}(\text{OH})_5] \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{PO}_4$  (see section 4.1, "Tetrahedral borophosphates"). The exchange of a borate triangle against a phosphate tetrahedron is observed in



**Fig. 24** Formation of an oB dreier-single ring  $\Delta 4\Box:\Box<\Delta 2\Box>\Box$  (B:P = 2:3) by condensation of the BBUs  $\Delta\Box$  (B:P = 1:1) and  $3\Box:3\Box$  (B:P = 1:2) via two common oxygen atoms.

other structural patterns as well (see Fig. 27). As shown in Figure 20, the tetrahedral heptamer  $7\Box:[<3\Box>]\Box\Box\Box\Box$  (B:P = 2:5) consists of the BBUs with B:P = 1:2 (uB trimer,  $3\Box:3\Box$ ) and 1:3 (oB tetramer,  $4\Box:[\Box]\Box\Box\Box$ ), respectively. Accordingly, the mixed-branched heptamer likewise originates from the uB tetrahedral trimer ( $3\Box:3\Box$ ) and a mixed-coordinated oB tetramer  $4\Box:[\Box]\Box\Box\Box$  which is hitherto unknown.

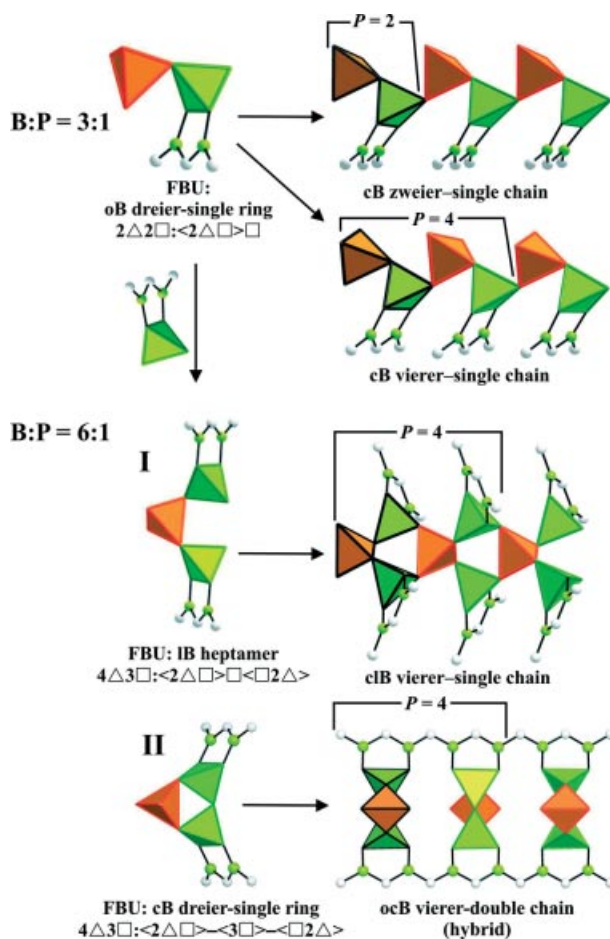


**Fig. 25** The mixed-coordinated open-branched ring-anion  $\Delta 6\Box:[<\Delta 2\Box>]\Box\Box\Box\Box$  (left) and its tetrahedral analogue (right, B:P = 2:5) are both part of a heteropolyoxocluster (including the VO group). The borate triangle and the phosphate tetrahedron occupy equivalent positions in the three-membered ring motif.

### B:P = 6:1–3:2

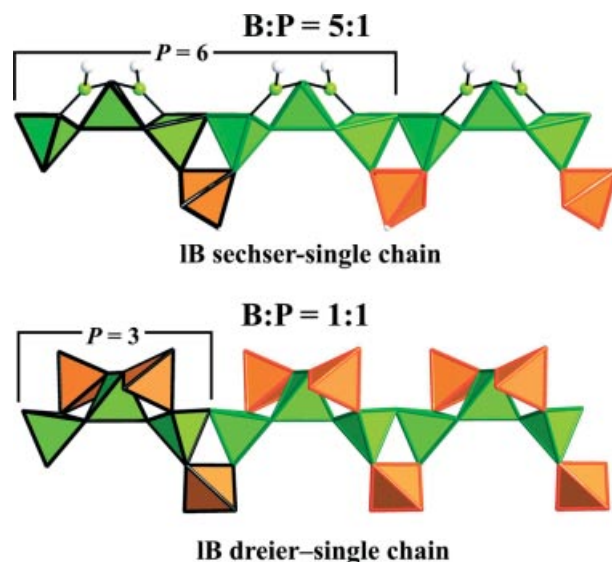
In the compounds with high borate content (B:P = 3:2, 3:1, 5:1 and 6:1) only anions with a dimensionality  $D = 1$  have been observed to date. A summary of the corresponding compounds is given in Table 20. Remarkable is the fact that all borophosphates with B:P > 1:1 known to date are mixed-coordinated. The compounds under consideration are usually synthesized hydrothermally and contain protonated partial structures. Only  $\text{Na}_3[\text{B}_6\text{PO}_{13}]$  was obtained from a flux and comprises non-protonated borophosphate

anions. On search for the FBUs of these borophosphate strands, discrete fragments exclusively consisting of borate units are dominating the structural patterns with increasing B:P ratio. Focusing for instance on mixed coordinated borophosphates with B:P = 3:1 and 6:1, the compounds contain dreier-single borate rings  $\langle 2\Delta\Box \rangle$  in different connection patterns as shown in Figure 26. The crystal structures  $(\text{NH}_4)_2[\text{B}_3\text{PO}_7(\text{OH})_2]$  and  $\text{Li}[\text{B}_3\text{PO}_6(\text{OH})_3]$  comprise cB single-chains with different periodicity (Fig. 26, top, B:P = 3:1) in which the  $\langle 2\Delta\Box \rangle$  rings alternate with  $\text{P}^{2/4}$  units. The corresponding FBU of these chain anions, an open-branched dreier-single ring  $2\Delta 2\Box : \langle 2\Delta\Box \rangle \Box$ , is shown in the left part of Figure 26 (top).



**Fig. 26** Mixed coordinated borophosphate anions with B:P = 3:1 and 6:1 comprise borate rings  $\langle 2\Delta\Box \rangle$  as common structural feature. The partial structures with B:P = 3:1 (top) comprise cB single-chains consisting of open-branched ring FBUs  $\langle 2\Delta\Box \rangle \Box$ . With B:P = 6:1 (bottom) two different chain motifs (I, II) have been observed in which the number of borate rings  $\langle 2\Delta\Box \rangle$  is doubled. The corresponding FBUs are expanded by one of the borate rings. Whereas in the cB vierer-single chain (I) only the tetrahedra contribute to the extension of the anion, the ocB vierer-double chains (II) propagate via the borate triangles.

With a ratio B:P = 6:1, the number of borate rings is doubled in the crystal structures of  $\text{K}[\text{B}_6\text{PO}_{10}(\text{OH})_4]$  (Fig. 26, I) and  $\text{Na}_3[\text{B}_6\text{PO}_{13}]$  (Fig. 26, II) which both comprise



**Fig. 27** Loop-branched sechser-single chains in the crystal structure of  $\text{K}_3[\text{B}_5\text{PO}_{10}(\text{OH})_3]$  (B:P = 5:1, top) are closely related to chains found in the crystal structures of the stillwellite analogous borophosphates  $M^{\text{II}}[\text{BPO}_5]$  (bottom, B:P = 1:1). Borate triangles and phosphate tetrahedra are found on equivalent positions in the loop-branched motifs. The FBUs of the chains are highlighted by black edges.

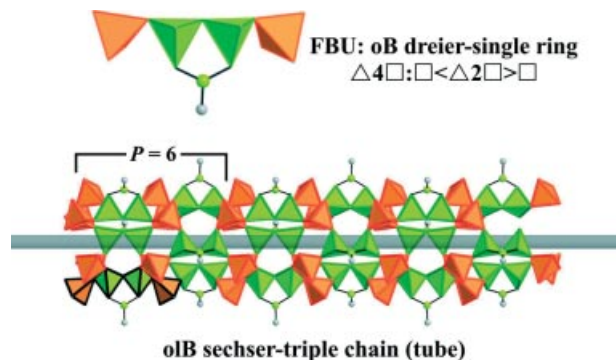
unique borophosphate chains. In case of  $\text{K}[\text{B}_6\text{PO}_{10}(\text{OH})_4]$  the chain motif can be derived from the borophosphate chains with B:P = 3:1 (Fig. 26, top): Four-membered rings are formed along the chain by formally condensing the tetrahedra of the additional borate rings. By this, the connectedness of the phosphate tetrahedra is increased to  $\text{P}^{4/4}$ . The resulting structural motif is a cB vierer-single chain (Fig. 26, I). The ocB vierer-double chain as observed in the crystal structure of  $\text{Na}_3[\text{B}_6\text{PO}_{13}]$  propagates via the trigonal-planar borate groups which form the backbones of the double chain (Fig. 26, II). As the phosphate tetrahedra may as well be assigned to one of the strands when defining the fundamental chain, the term hybrid may be used as proposed for silicates [2]. In contrast to the aforementioned compounds the borate triangles are non-protonated and contribute to the extension of the anion. The FBUs of the chain anions with B:P = 6:1 can be obtained by formally condensing the FBU with B:P = 3:1 (open-branched dreier-single ring  $2\Delta 2\Box : \langle 2\Delta\Box \rangle \Box$ ) with another three-membered borate ring. Whereas the loop-branched heptameric FBU of  $\text{K}[\text{B}_6\text{PO}_{10}(\text{OH})_4](4\Delta 3\Box : \langle 2\Delta\Box \rangle \Box \langle \Box 2\Delta \rangle)$ , I) is formed when the additional borate ring is linked to the phosphate group with one vertex of its tetrahedral member, a cB dreier-single ring  $(4\Delta 3\Box : \langle 2\Delta\Box \rangle - \langle 3\Box \rangle - \langle \Box 2\Delta \rangle)$ , II) as FBU results if another oxygen atom is shared in a B–O–B connection.

The crystal structure of  $\text{K}_3[\text{B}_5\text{PO}_{10}(\text{OH})_3]$  (B:P = 5:1) comprises loop-branched sechser-single chains as shown in Figure 27 (top). The backbone of the chains consists of borate tetrahedra ( $\text{B}^{4/4}$ ), the loop-branches contain borate triangles ( $\text{B}^{2/3}$ ) and phosphate tetrahedra ( $\text{P}^{2/4}$ ). As there



are twice as many  $B\Phi_3$  units compared to phosphate tetrahedra, each third branch contains a phosphate group. The strands show a close relationship to the stillwellite analogous borophosphates  $M^{\text{II}}[\text{BPO}_5]$  (B:P = 1:1) which comprise only tetrahedral phosphate branches (Fig. 27, bottom). As already shown for two closely related clusters (Fig. 25), borate triangles and phosphate tetrahedra can be found on equivalent positions in cyclic motifs. This formal exchangeability of borate triangles and phosphate tetrahedra, and the fact that similar chains are also known in borates [4, 5] indicate that further chains with varying B:P should exist. The FBU of the mixed coordinated sechser-single chain is supposed to be heptamer. The exact sequence of polyhedra in the FBU can not unambiguously be given but a sequence  $2\Delta 4\Box < \Delta 2\Box > - < 2\Box \Delta > \Box$  (Fig. 27, highlighted by black edges) appears to be meaningful as it pronounces the presence of three-membered borate rings which are typical for borates.

Two borophosphates have been reported with B:P = 3:2:  $\text{Na}_2M^{\text{II}}[\text{B}_3\text{P}_2\text{O}_{11}(\text{OH})] \cdot 0.67\text{H}_2\text{O}$  and  $\text{Na}_5(\text{H}_3\text{O})M^{\text{II}}_3[\text{B}_3\text{P}_2\text{O}_{11}(\text{OH})]_3 \cdot 2\text{H}_2\text{O}$  which are possibly isotypes (see Table 20). The higher symmetry and the presence of  $\text{H}_3\text{O}^+$  ions in the latter compound leads to an incoherent structure comprising too short distances Na–Na and Na–O of 240 pm and 146 pm, respectively. Nevertheless, these compounds comprise a unique tube-like borophosphate partial structure (Fig. 28, bottom). Like a ring represents a special case of an oligomer due to the missing ends, a tube is exceptional for chains. As a layered anion with the same connectivity is also possible, the dimensionality of this special polymer is marked as  $D = 1(\text{tb})$ . These borophosphate anions are referred to oB dreier-single ring FBUs  $\Delta 4\Box < \Box < \Delta 2\Box > \Box$  (Fig. 28, top) and have to be denoted as oB sechser-triple chains. The close relation with the tetrahedral FBU  $5\Box < \Box < 3\Box > \Box$  (B:P = 2:3, Figures 9 and 10) again shows the equivalence of borate triangles and phosphate tetrahedra in three-membered ring motifs.



**Fig. 28** Unbranched sechser-triple chains (tubes) observed in crystal structures of mixed-coordinated borophosphates with B:P = 3:2 (Table 20). The corresponding FBU is an oB dreier-single ring.

### 4.3 Metalloborophosphates

Up to date metalloborophosphates exclusively comprise three-dimensional anionic partial structures built of tetra-

**Table 20** Mixed-coordination chains in (pseudo-)alkali metal borophosphates with B:P = 3:2–6:1.

B:P = 3:2		Chains $\frac{1}{2}\{\text{B}_3\text{P}_2\Phi_{12}\}_m$ ( $\Phi = \text{O, OH}$ ) ( $m = 2$ ) $D = 1(\text{tb}); M = 3; \mathcal{Q}^{m/\text{CN}}; \text{B}^{2/3}, \text{B}^{4/4}, \text{P}^{2/4}$		
O:OH	Compound	SG	Synth.	Ref.
11:1	$\text{Na}_2M^{\text{II}}[\text{B}_3\text{P}_2\text{O}_{11}(\text{OH})] \cdot 0.67\text{H}_2\text{O}$ $M^{\text{II}} = \text{Cu}$	$P6_3/m$ (No. 176)	F	[129]
	$M^{\text{II}} = \text{Mg, Mn-Zn}$	$P6_3$ (No. 173)	H	[130]
	$\text{Na}_5(\text{H}_3\text{O})M^{\text{II}}_3[\text{B}_3\text{P}_2\text{O}_{11}(\text{OH})]_3 \cdot 2\text{H}_2\text{O}$ $M^{\text{II}} = \text{Mg, Mn-Zn}$	$P6_3/m$ (No. 176)	H	[131]
B:P = 3:1		Chains $\frac{1}{3}\{\text{B}_3\text{P}\Phi_9\}_m$ ( $\Phi = \text{O, OH}$ ) ( $m = 1, 2$ ) $D = 1; M = 1; \mathcal{Q}^{m/\text{CN}}; \text{B}^{2/3}, \text{B}^{4/4}, \text{P}^{2/4}$		
O:OH	Compound	SG	Synth.	Ref.
11:3	$(\text{NH}_4)_2[\text{B}_3\text{PO}_7(\text{OH})_2]$	$P2_1/c$ (No. 14)	H	[132]
	$\text{Li}[\text{B}_3\text{PO}_6(\text{OH})_3]$	$Pbcn$ (No. 60)	H	[133]
B:P = 5:1		Chains $\frac{1}{5}\{\text{B}_5\text{P}\Phi_{13}\}_m$ ( $\Phi = \text{O, OH}$ ) ( $m = 2$ ) $D = 1; M = 1; \mathcal{Q}^{m/\text{CN}}; \text{B}^{2/3}, \text{B}^{4/4}, \text{P}^{2/4}$		
O:OH	Compound	SG	Synth.	Ref.
10:3	$\text{K}_3[\text{B}_5\text{PO}_{10}(\text{OH})_3]$	$P2/c$ (No. 13)	H	[134]
B:P = 6:1		Chains $\frac{1}{6}\{\text{B}_6\text{P}\Phi_{14}\}_m$ ( $\Phi = \text{O, OH}$ ) ( $m = 2$ ) $D = 1; M = 1; \mathcal{Q}^{m/\text{CN}}; \text{B}^{2/3}, \text{B}^{4/4}, \text{P}^{2/4}$		
O:OH	Compound	SG	Synth.	Ref.
5:2	$\text{K}[\text{B}_6\text{PO}_{10}(\text{OH})_4]$	$P4/ncc$ (No. 130)	H	[135]
B:P = 6:1		Chains $\frac{1}{6}\{\text{B}_6\text{P}\Phi_{13}\}_m$ ( $\Phi = \text{O, OH}$ ) ( $m = 2$ ) $D = 1; M = 2; \mathcal{Q}^{m/\text{CN}}; \text{B}^{3/3}, \text{B}^{4/4}, \text{P}^{2/4}$		
O:OH	Compound	SG	Synth.	Ref.
1:0	$\text{Na}_3[\text{B}_6\text{PO}_{13}]$	$Pnma$ (No. 62)	F	[105]

hedra which are unique to a ratio of metallate, borate, and phosphate polyhedra of  $M:\text{B}:\text{P} = 1:1:2$ . Only a series of metalloborophosphates deviating from this composition has been reported to comprise a  $M:\text{B}:\text{P}$  ratio of 2:1:3:  $(\text{NH}_4)_{16}[\text{M}_{16}\text{B}_8\text{P}_{24}\text{O}_{96}]$  ( $M = \text{Zn, Zn}_{1-x}\text{Co}_x$ ) [136], but the refined crystal structures comprise boron and the transition metals in a mixed occupancy resulting in B–O distances of 160 pm–182 pm which are significantly too large. Due to this, and the observed splitting of atomic positions in combination with exceptionally large displacement parameters the presented structures appear incoherent. The crystal structure of  $\text{Zn}[\text{BPO}_4(\text{OH})_2]$  likewise comprises a framework of zincate, borate and phosphate tetrahedra with a deviating composition ( $M:\text{B}:\text{P} = 1:1:1$ ) but it is not classified as a zincoborophosphate (see section 4.4, “Anion-substituted compounds and border-cases”).

In the well-defined crystal structures the metallate tetrahedra are centered by  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Be}^{2+}$  specimens. Remarkable in this group of compounds is the existence of anionic partial structures with zeolite or related topologies in which the tetrahedral units are interconnected in alternating fashion forming four-, six-, and eight-membered ring motifs, enclosing cavities and channels. In none of the partial structures bridging oxygen atoms between equal tetrahedral specimens (B–O–B, P–O–P, M–O–M) have been

observed so far, likewise no M–O–B connections exist to date. Thus, the interconnection schemes comprises borate and metallate tetrahedra only linked to phosphate ones and phosphate specimen connected with two borate and two metallate units. Removing the metallate tetrahedra, the remaining borophosphate partial structures and structural motifs strictly agree with those observed for borophosphates with B:P = 1:2 (see section 4.1, B:P = 1:2).

All known metalborophosphates can be referred to a common FBU which is the dominant structural motif of all compounds: an unbranched (uB) vierer-single ring  $4\Box:\langle 4\Box\rangle$  consisting of two phosphate groups connected via one metallate and one borate tetrahedron (denoted as MPBP, see Fig. 29).



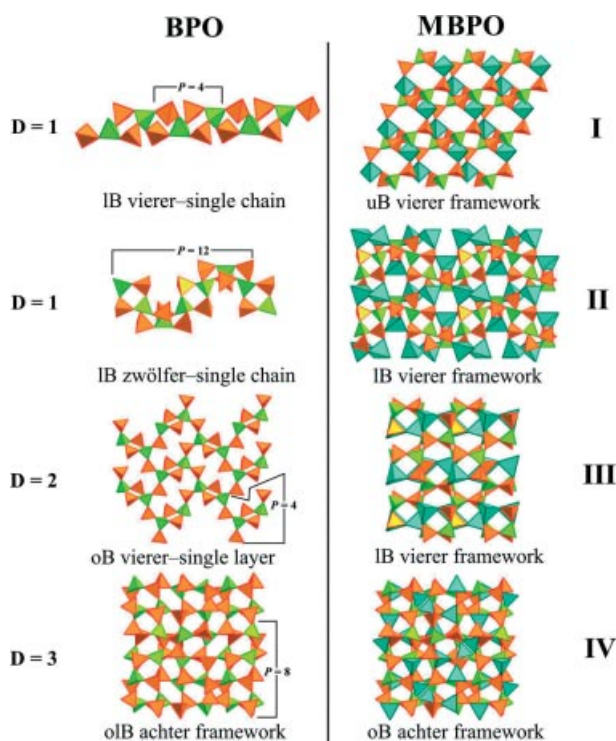
**Fig. 29** An unbranched vierer-single ring  $[\text{MBP}_2\Phi_{13}]$  (MPBP) represents the common fundamental building unit of metalborophosphate partial structures.

As already stated, the FBUs are interconnected obeying certain connection rules. These allow the formation of further four-membered ring motifs in which the rings either consist of two phosphate and two borate tetrahedra (BPBP) or two metallate and two phosphate tetrahedra (MPMP). All known metalborophosphates contain framework anions with the same composition  $M:\text{B}:\text{P} = 1:1:2$ , but the resulting topologies are different depending on the way the FBUs are interconnected. As the metalborophosphates differ in the dimensionality of the borophosphate partial structures, they can be assorted according to this criterion, as shown in Figure 30. In the same order all existing metalborophosphates are summarized in Table 21.

The metalborophosphates were synthesized hydrothermally with the exception of one  $\text{NH}_4[\text{ZnBP}_2\text{O}_8]$  polymorph which was obtained solvothermally using ethylene glycol as a solvent, and of  $\text{Na}[\text{ZnBP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ , a dehydration product of the helical borophosphate  $\text{NaZn}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8]\cdot\text{H}_2\text{O}$  (see section 4.1, “Borophosphates with B:P = 1:2”).

In the crystal structures of the isotypic compounds  $A^I[\text{ZnBP}_2\text{O}_8]$  ( $A^I = \text{NH}_4, \text{Rb}, \text{Cs}$ ) and the partially substituted phase  $\text{NH}_4[(\text{Zn}_{1-x}\text{Co}_x)\text{BP}_2\text{O}_8]$  ( $0 \leq x \leq 0.4$ ), loop-branched borophosphate chains (vierer-single) are interconnected by metallate tetrahedra forming an unbranched vierer framework (built from uB MBPO double chains) with gismondine topology (Fig. 30, I) which comprises both MPMP and BPBP rings besides the FBU motif MPBP. The zincborophosphates  $\text{Na}[\text{ZnBP}_2\text{O}_8]\cdot\text{H}_2\text{O}$ ,

$(\text{C}_4\text{N}_3\text{H}_{16})[\text{Zn}_3\text{B}_3\text{P}_6\text{O}_{24}]\cdot\text{H}_2\text{O}$ , and  $(\text{C}_6\text{N}_4\text{H}_{22})_{1.5}\text{[Zn}_6\text{B}_6\text{P}_{12}\text{O}_{48}]\cdot 1.5\text{H}_2\text{O}$  contain a loop-branched vierer framework with CZP topology (Fig. 30, II). The cyclic FBUs (MPBP) are interconnected via the borate and phosphate tetrahedra forming loop-branched zwölfer-single chains with helical conformation (BPBP motif). These strands are linked by the zincate tetrahedra forming the chiral framework in analogy to the large group of helical borophosphates where the helices are linked by coordination octahedra (see section 4.1, Tetrahedral borophosphates with B:P = 1:2). Focusing on the borophosphate anions the only difference from the loop-branched vierer-single chains mentioned above (type I) is found in the conformation of the strands. Both borophosphate chains hierarchically descend from the open-branched vierer-single rings  $6\Box:\langle 4\Box\rangle\Box$  (FBU) representing the essential structural motif.



**Fig. 30** Tetrahedral frameworks of the known metalborophosphates (right), assorted according to the dimensionality of the borophosphate partial structure (left). The corresponding compounds are summarized in Table 21.

The anhydrous zincborophosphates  $A[\text{ZnBP}_2\text{O}_8]$  ( $A = \text{NH}_4, \text{K}$ ) comprise an anionic framework with the same composition like the aforementioned compounds but the interconnection scheme of the FBUs (MPBP) in this case leads to a topology related to feldspars (Fig. 30, III). The corresponding layered borophosphate partial structure is likewise built from open-branched vierer-single rings  $6\Box:\langle 4\Box\rangle\Box$ .

In the crystal structures of the isotypic beryllborophosphates  $A[\text{BeBP}_2\text{O}_8]\cdot x\text{H}_2\text{O}$  ( $A = \text{Na}^+, \text{K}^+, \text{NH}_4^+$ ) an open-branched achterframework with analcime topology is found (Fig. 30, IV). In the three-dimensional arrangement of

tetrahedra, no further four-membered ring motifs are formed, instead the FBUs are interconnected forming six- and eight-membered ring apertures. Focusing on the borophosphate partial structure, an open-branched achter framework is present, built of open-branched six-membered rings  $9\Box:\Box<6\Box>\Box|\Box|\Box$  known as one of the FBUs of borophosphates with B:P = 1:2 (see section 4.1, Tetrahedral borophosphates with B:P = 1:2). Another striking aspect of these structures is that the borophosphate and beryllorophosphate frameworks are identical.

**Table 21** Metalloborophosphates with M:B:P = 1:1:2 containing anionic frameworks built from tetrahedra (For corresponding framework types I-IV see Fig. 30).

$D_{\text{BPO}}$	O:OH	Compound /	Framework $\frac{3}{2}[\text{MBP}_2\Phi_8]$ ( $\Phi = \text{O}, \text{OH}$ )		Synth.	Ref.
			SG			
1 Type I	1:0	$A^1[\text{ZnBP}_2\text{O}_8]$	$P\bar{1}$ (No. 2)		H	[137]
		$A^1 = \text{NH}_4, \text{Rb}, \text{Cs}$ $\text{NH}_4[(\text{Zn}_{1-x}\text{Co}_x)\text{BP}_2\text{O}_8]$ ( $0 \leq x \leq 0.4$ )				H
1 Type II	1:0	$\text{Na}[\text{ZnBP}_2\text{O}_8] \cdot \text{H}_2\text{O}$	$P6_122$ (No. 178)	H	[139]	
		$(\text{C}_4\text{N}_3\text{H}_{16})[\text{Zn}_3\text{B}_3\text{P}_6\text{O}_{24}] \cdot \text{H}_2\text{O}$	$P6_522$ (No. 179)	H	[140]	
		$(\text{C}_6\text{N}_4\text{H}_{22})_{1.5}[\text{Zn}_6\text{B}_6\text{P}_{12}\text{O}_{48}] \cdot 1.5\text{H}_2\text{O}$	$P6_522$ (No. 179)	H	[141]	
2 Type III	1:0	$A^1[\text{ZnBP}_2\text{O}_8]$	$C2/c$ (No.15)	H	[137, 142]	
		$A^1 = \text{NH}_4, \text{K}$				
3 Type IV	1:0	$A[\text{BeBP}_2\text{O}_8] \cdot x\text{H}_2\text{O}$ $A = \text{Na}^+, \text{K}^+, \text{NH}_4^+$	$P2_13$ (No. 198)	H	[143]	

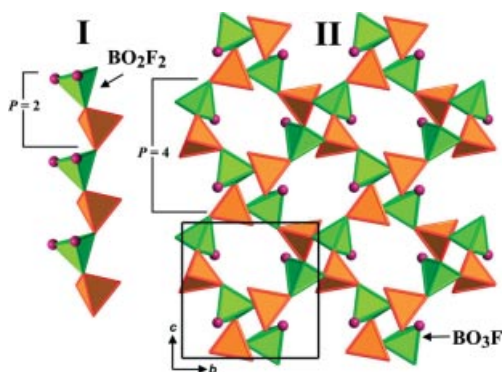
#### 4.4 Anion-substituted compounds and border-cases

Up to date only a small number of (metallo)borophosphates is known in which the oxoligands of the complex anions are substituted. The structures will be discussed in detail in the following, a summary of all compounds is given in Table 22.

**Table 22** Anion-substituted (metallo)borophosphates and special cases known to date.

Anion-substituted Borophosphates					
B:P	Compound	SG	Synth.	Ref.	
1:1	$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{BPO}_4\text{F}_2]$	$P\bar{1}$ (No. 2)	H	[146]	
1:1	$(\text{NH}_4)[\text{BPO}_4\text{F}]$	$P2_1/3$ (No. 198)	F	[147]	
1:4	$(\text{ImH}_2)[\text{Mo}^{\text{V}}_5\text{Mo}^{\text{VI}}_7\text{O}_{30}(\text{BPO}_4)_2(\text{O}_3\text{P-Ph})_6]$	$P2_1/c$ (No. 14)	H	[148]	
Metalloborophosphates					
B:P	Compound	SG	Synth.	Ref.	
1:2	$(\text{C}_6\text{H}_{14}\text{N}_2)\{\text{Zn}[\text{ZnB}_2\text{P}_4\text{O}_{15}(\text{OH})_2] \cdot (\text{C}_6\text{H}_{13}\text{N}_2)\text{Cl}\}$	$P2_1/c$ (No. 14)	H	[149]	
Special cases					
B:P	Compound	SG	Synth.	Ref.	
1:2	$\text{Zn}[\text{BPO}_4(\text{OH})_2]$	$Pbcn$ (No. 60)	H	[150]	

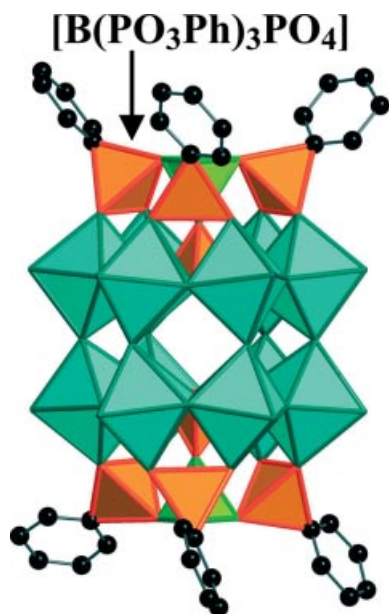
Two fluorine substituted compounds with different degree of fluorination have been reported:  $(\text{NH}_4)[\text{BPO}_4\text{F}]$  and  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{BPO}_4\text{F}_2]$ . In both cases substitution is observed at the borate tetrahedra. Fluoride ligands are non-bridging and, thus, have a strong influence on the dimensionality of the anionic partial structures formed. The crystal structure of  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{BPO}_4\text{F}_2]$  comprises uB zweier-single chains of alternating phosphate and di-substituted borate tetrahedra (Fig. 31, I). As the  $[\text{BO}_2\text{F}_2]$  units allow at maximum two connections ( $B^{2/4}$ ) and condensation of phosphate groups is avoided, a chain represents the anion with the highest possible dimensionality for the composition B:P = 1:1. Mono-substituted borate tetrahedra  $[\text{BO}_3\text{F}]$  comprise only one terminal vertex and can, thus, have a connectedness of  $B^{3/4}$ . This allows the anionic partial structure of  $(\text{NH}_4)[\text{BPO}_4\text{F}]$  to have a dimensionality  $D = 3$ , although having the same B:P ratio of 1:1. The framework is built of alternating  $[\text{PO}_4]$  and  $[\text{BO}_3\text{F}]$  tetrahedra and comprises a zeolite-like topology (gismondine), as shown in Figure 31 (II). Both anionic partial structures,  $\frac{1}{2}[\text{BPO}_4\text{F}_2]$  and  $\frac{3}{2}[\text{BPO}_3\text{F}]$  hierarchically originate from unbranched dimers  $2\Box:2\Box$



**Fig. 31** Fluorine substituted borophosphate anions (B:P = 1:1) in the crystal structures of  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{BPO}_4\text{F}_2]$  (uB zweier-single chain, I) and  $(\text{NH}_4)[\text{BPO}_4\text{F}]$  (uB vierer framework, II): Whereas the di-substituted  $[\text{BO}_2\text{F}_2]$  tetrahedra limit the dimensionality of the borophosphate anion to  $D = 1$ , the mono-substituted  $[\text{BO}_3\text{F}]$  groups in the crystal structure of  $(\text{NH}_4)[\text{BPO}_4\text{F}]$  allow the formation of a 3D framework.

With the crystal structure of  $(\text{ImH}_2)[\text{Mo}^{\text{V}}_5\text{Mo}^{\text{VI}}_7\text{O}_{30}(\text{BPO}_4)_2(\text{O}_3\text{P-Ph})_6]$  (Im = imidazole) a phenyl-substituted heteropolyoxo-compound has been reported. As shown in Fig. 32, the crystal structure comprises six-membered double-rings of  $\text{MoO}_6$  octahedra, each capped by two open-branched oligomers  $[\text{B}(\text{PO}_4)(\text{PO}_3\text{Ph})_3]$  ( $5\Box:\Box|\Box|\Box|\Box|\Box$ ). Strictly following the definition of borophosphates, the compound can not be denoted a borophosphate as the phosphorous atoms in the three phenylphosphonate tetrahedra do not have the oxidation state +5. Corresponding clusters are known with unsubstituted borophosphate ligomers  $5\Box:\Box|\Box|\Box|\Box|\Box$  (see section 4.1, B:P = 1:4).

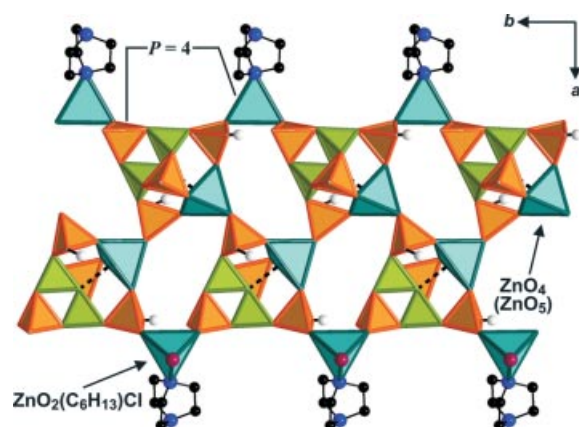
The crystal structure of  $(\text{C}_6\text{H}_{14}\text{N}_2)\{\text{Zn}[\text{ZnB}_2\text{P}_4\text{O}_{15}(\text{OH})_2] \cdot (\text{C}_6\text{H}_{13}\text{N}_2)\text{Cl}\}$  which has been described as zincoborophosphate containing ribbons of tetrahedra (see Fig. 33) represents another border-case in terms of structural



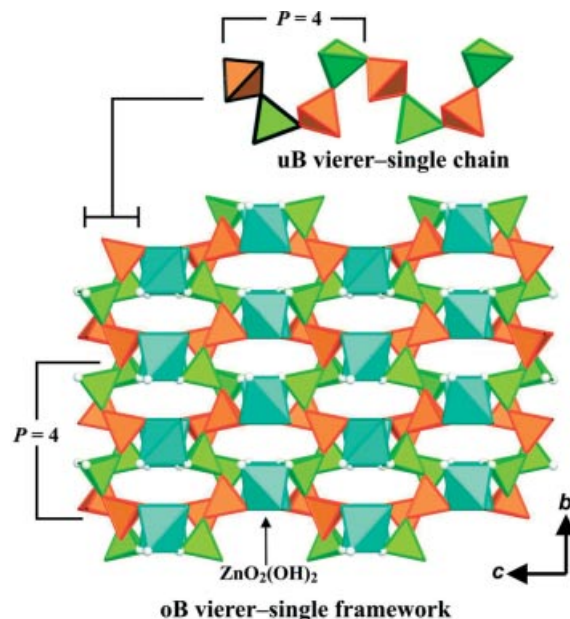
**Fig. 32** Heteropolyoxocluster in the crystal structure of  $(\text{ImH}_2)[\text{Mo}_5\text{Mo}_7\text{O}_{30}(\text{BPO}_4)_2(\text{O}_3\text{P-Ph})_6]$ : Six-membered double-rings of  $\text{MoO}_6$  octahedra are capped by open-branched tetrahedral pentamers  $5\Box:[\Box]\Box[\Box]\Box[\Box]$ . Corresponding clusters are known with unsubstituted phosphate(V) tetrahedra.

systematics. The partial structure has to be denoted as anion-substituted metalborophosphates due to the fact, that at one of the zinc sites two oxo-ligands are substituted by chloride and the organic amine, respectively. A closer look at the coordination sphere of the second zinc site furthermore shows a 4+1 coordination (longer distance indicated by dashed lines in Fig. 33). As any coordination number  $CN > 4$  would disagree with the definition of a metalborophosphate, the anionic partial structure can not clearly be described as ribbons of tetrahedra (but as mixed-branched vierer-single chains). Thus, a description as anion-substituted zinc-zincoborophosphate appears to be more appropriate. Nevertheless, just focusing on the borophosphate part, a mixed-branched (oB) dreier-single ring  $6\Box:[\lt 3\Box\gt]=\lt 3\Box\gt[\Box]\Box$  is present which has already been observed as FBU in the structural hierarchy of tetrahedral borophosphates with B:P = 1:2 (see section 4.1, Tetrahedral borophosphates with B:P = 1:2). This FBU is formed by condensation of two unbranched trimeric BBUs  $3\Box:3\Box$  sharing three common vertices. As none of the borate tetrahedra contains unshared oxygen vertices the FBUs  $6\Box:[\lt 3\Box\gt]=\lt 3\Box\gt[\Box]\Box$  may not form borophosphate partial structures of higher dimensionality due to the avoidance of oxygen bridges between phosphate tetrahedra.

The crystal structure of  $\text{Zn}[\text{BPO}_4(\text{OH})_2]$  comprises unbranched vierer-single chains of alternating phosphate and dihydrogen borate tetrahedra (B:P = 1:1, Fig. 34, top) which are interconnected by zinc which is likewise fourfold coordinated by oxygen ( $\text{ZnO}_2(\text{OH})_2$ ) forming a framework with moganite [144, 145] topology (oB vierer framework, Fig. 34, bottom). Although zinc is tetrahedrally coordi-



**Fig. 33** The anionic partial structure of  $(\text{C}_6\text{H}_{14}\text{N}_2)\{\text{Zn}[\text{ZnB}_2\text{P}_4\text{O}_{15}(\text{OH})_2]\cdot(\text{C}_6\text{H}_{13}\text{N}_2)\text{Cl}\}$  has to be described as anion-substituted zincoborophosphate containing  $[\text{ZnO}_2(\text{C}_6\text{H}_{13}\text{N}_2)\text{Cl}]$  tetrahedra. The second Zn site comprises a 4+1 coordination by oxygen atoms and should therefore not be regarded as part of the anionic partial structure ( $CN > 4$ ). The borophosphate oligomers (oB dreier-single rings,  $6\Box:[\lt 3\Box\gt]=\lt 3\Box\gt[\Box]\Box$ ) are known members in the hierarchy of tetrahedral anions with B:P = 1:2 (for further details see text).



**Fig. 34** In the crystal structure of  $\text{Zn}[\text{BPO}_4(\text{OH})_2]$  borophosphate chains (uB vierer-single chains, top) are interlinked by zincate tetrahedra forming an open-branched vierer framework with moganite topology (bottom). As the framework is neutral, zinc can't be counted as part of the anionic partial structure. The compound should be classified as tetrahedral borophosphate (B:P = 1:1) rather than as metalborophosphate.

nated, it can not be counted as part of the anionic partial structure as the resulting framework is neutral. Thus, the compound is not classified as a metalborophosphate but as a special case of tetrahedral borophosphates with B:P = 1:1. The unbranched borophosphate chains are known from

a series of other compounds as summarized in Table 3 (section 4.1, “Tetrahedral borophosphates”).

#### 4.5 Borate-phosphates

The group of borate-phosphates comprises isolated borate and phosphate species ( $[B\Phi_3]$ ,  $[B\Phi_4]$ ,  $[P\Phi_4]$ ), additionally further oxide- or hydroxide-ions may be present in the compounds like in the series of lanthanoid oxo-borate-phosphates  $Ln_7O_6[BO_3][PO_4]_2$  ( $Ln = La, Pr, Nd, Sm, Gd, Dy$ ). All borate-phosphates with the corresponding references known to date are summarized in Table 23.

**Table 23** Borate-phosphates containing isolated borate and phosphate anions.

B:P	Compound	Isolated $[B\Phi_3]$ , $[P\Phi_4]$ ( $\Phi = O, OH$ ) $D = 0, M = 1, Q^{m/cn}; B^{0/3}, P^{0/4}$	
		SG	Synth. Ref.
1:1	$M^{II}_3[BO_3][PO_4]$ $M^{II} = Zn^{2+}$	$P\bar{6}m2$ (No. 187), $P\bar{6}2m$ (No. 189), $Immm$ (No. 71), $Cm$ (No. 8)	S [151, 152]
	$M^{II} = Mg^{2+}$	$P\bar{6}m2$ (No. 187), $P\bar{6}2m$ (No. 189), $Immm$ (No. 71)	S, H [151, 153]
	$M^{II} = Co$	$Cm$ (No. 8)	F [154]
1:2	$Ln_7O_6(BO_3)(PO_4)_2$ ( $Ln = La, Pr, Nd, Sm, Gd, Dy$ )	$P2_1/n$ (No. 13)	S, F [155–157]

B:P	Compound	Isolated $[B\Phi_4]$ , $[P\Phi_4]$ ( $\Phi = O, OH$ ) $D = 0, M = 1, Q^{m/cn}; B^{0/4}, P^{0/4}$	
		SG	Synth. Ref.
1:1	$Mn_3(OH)_2[B(OH)_4][PO_4]$	$Pbnm$ (No. 62)	N [158–160]

<sup>a)</sup> High and low temperature forms with different spacegroups have been reported. The assignment of  $\alpha$ - and  $\beta$ -phase is not clear at present.

As the presented classification is based on a hierarchical condensation scheme, isolated polyhedra correspond to the lowest hierarchy level and can only be classified according to the number and ratio of complex anions present in the crystal structures. The compounds were mainly synthesized by solid-state syntheses or with a flux, but can also be obtained hydrothermally as shown for  $Mg_3[BO_3][PO_4]$ . The mineral Seamanite,  $Mn_3(OH)_2[B(OH)_4][PO_4]$ , likewise belongs to this group of compounds

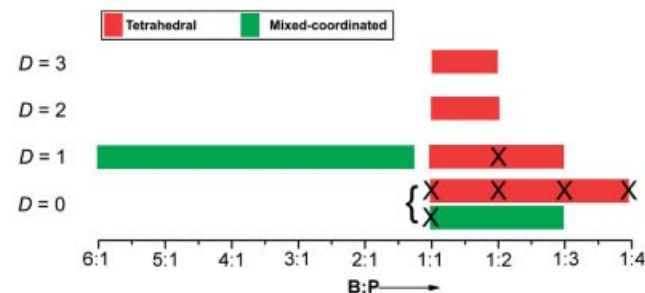
## 5 Summary and Conclusion

Within the past twelve years the group of (metallo)borophosphates has grown steadily and numerous compounds are known to date comprising a large structural variety. Combining and extending classification principles for (alumo)silicates and borates and following the first approach on borophosphate structural chemistry given in 1998, a hierarchical classification scheme for borophosphates and metalloborophosphates has been proposed, assuming simple oligomeric building units. The formalism of anionic partial structures to be built from basic building units (BBUs) and fundamental building units (FBUs) is a helpful tool for

basic understanding of structure formation and appearance of structural patterns controlled by interconnection rules.

By this means tetrahedral borophosphates could be hierarchically ordered according to the composition (BBUs) and the essential structural motif (FBUs) of the anionic partial structures. As shown in this overview of all compounds known to date, certain B:P ratios appear more frequently than others and borate and phosphate units are not interlinked arbitrarily. Hence, certain structural patterns are dominant and some anions are observed in numerous compounds (e.g. helical chains with B:P = 1:2). Besides open-branches especially three-, four-, and six-membered rings predominantly appear as structural motifs.

Especially the avoidance of P–O–P bonds and, thus, the composition B:P, is of strong structural influence. The terminal character of the phosphate groups limits the dimensionality of the borophosphate partial structures with increasing phosphate content (decreasing B:P) and leads to open-branched motifs as well as to the appearance of isolated (additional) phosphate units. This influence is shown in Fig. 35 in which the observed dimensionalities of the borophosphate anions is shown as a function of the composition B:P. Furthermore, compositions and dimensionalities of borophosphates containing isolated phosphate specimens are indicated by black crosses. Like this it can be shown that up to date additional phosphate units preferably exist beside low dimensional borophosphate partial structures ( $D \leq 1$ ) with a molar ratio B:P  $\leq 1:1$ .



**Fig. 35** Dimensionality of borophosphate partial structures; mixed coordinated (green) and tetrahedral (red). Composition and dimensionality of compounds with additional isolated phosphate groups are marked with crosses.

The regions of existence of tetrahedral borophosphates with a certain dimensionality ( $D = 1 - 3$ ) are marked in red and include the borophosphate partial structures of metalloborophosphates. The graph illustrates that frameworks and layers are only observed in a small range of composition between 1:1 and 1:2. With decreasing B:P the number of B–O–P bonds increases and, thus, more and more open-branches are found until a fully branched pentamer  $[BP_4\Phi_{12}]$  with B:P = 1:4 results which can not be interlinked to higher-dimensional arrangements. Furthermore it can be read from Figure 35 that tetrahedral borophosphates have just been observed with B:P ratios between 1:1 and 1:4. All borate rich compounds known to date comprise

mixed coordinated anions (green). In all the known compounds OH-groups are terminal. Exceptions of this observation may be found for bridging oxygen atoms between two borate units which could be protonated like observed in the crystal structures of borates [4, 5]. Future experimental results have to show to what extent these observations are valid as general rules. Crystalline phases obtained by differing methods of preparation or reaction conditions may lead to results that disagree with the observed regularities.

In the case of metalloborophosphates and of mixed-coordinated borophosphates the number of known phases is comparatively small what hampers a detailed classification. Nevertheless, it could be shown that besides the avoidance of P–O–P bonds further rules seem to be relevant for the structure formation. Metalloborophosphates for instance show a strong limitation in composition and in their anionic partial structures no connections between equal tetrahedral specimens are found. The dominant structural motif is a four-membered ring of two phosphate groups interconnected by a borate and a metallate tetrahedron (MPBP). In mixed-coordinated borophosphates further building units are observed with the appearance of trigonal-planar borate groups. In the borate-rich compounds (B:P = 6:1-3:2) fragments just containing  $B\Phi_3$  and  $B\Phi_4$  units are relevant similar to the borate structural chemistry (especially three-membered rings). Why the dimensionality of the mixed-coordinated borophosphate anions is hitherto limited to  $D = 1$  (Fig. 35) remains unclear. A possible explanation for large B:P ratios may be found in the observation that trigonal planar borate units are mostly protonated and do not contribute to interconnection. Mixed-coordinated borophosphates with high phosphate content (B:P = 1:1–1:3) are hitherto only known with oligomeric anions. Besides the terminal character of phosphate tetrahedra with decreasing B:P ratio, a further reason for the limited dimensionality may be due to limited connections between phosphate tetrahedra and  $B\Phi_3$  units (in the known compounds phosphate groups are only connected to one borate triangle). As the number of metalloborophosphates and mixed-coordinated compounds is rather small to date future results have to show whether it is possible to find further principles that can be used in terms of structural systematics. The anion-substituted borophosphates presented in section 4.5 exemplify the existence of further, closely related compounds and likewise point out the border of the proposed structural systematic.

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