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A First Approach to Borophosphate Structural Chemistry

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Borophosphates (intermediate compounds of the system $M_xO_y-B_2O_3-P_2O_5-(H_2O)$) contain complex anionic structures built of BO_4, BO_3, and PO_4 groups and their partially protonated species, respectively. A first approach to the development of a structural chemistry of borophosphates is based on linking principles of the primary building units following the general line of silicate crystal chemistry. The crystal structures of borophosphates are first divided into anhydrous and hydrated phases. Further gradings are based on the (molar) B:P ratios. The structural chemistry of borophosphate anions already extends from isolated species, oligomers, rings, and chains to layers and frameworks. Additional characteristics are integration of planar BO_3 groups, preferred formation of 3-membered rings, and unusual branching of tetrahedral chains. P−O−P linking in borophosphates is not observed up to now.

Borophosphates are intermediate compounds of the systems $M_xO_y-B_2O_3-P_2O_5-(H_2O)$ which contain complex anionic structures built of BO_4, BO_3, and PO_4 groups and their partially protonated species, respectively. By this, there is a formal relation to the large group of alumophosphates[1a] (Al_2O_3 instead of B_2O_3). The polymorphous modifications of BPO_4[1b,c] are not under consideration in this paper. Although systematic investigations of borophosphates have been started only 5 years ago[2] numerous borophosphates and their crystal structures have already been reported up to now (M = Li, Na, K, (NH_4^+), Rb, Cs, Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn, Ag, Pb). A first approach to the development of a structural chemistry of borophosphates is based on the linking principles of the primary building units following the general line of silicate crystal chemistry.[3] The classification at this stage is exclusively focused on the anionic partial structures, although it is clear that the cations (charge, size, and coordination behavior) have a significant influence even on the dimensionality of the anionic structural units.

The crystal structures of borophosphates are first divided into anhydrous and hydrated phases. Further gradings are based on the (molar) B:P ratios. Borophosphates containing foreign anionic species besides the primary BO_4, BO_3, and PO_4 groups are not under consideration.[4] Today, the structural chemistry of borophosphate anions already extends from isolated species, oligomers, rings, and chains to layers and frameworks. The existing minority of compounds containing isolated borate besides isolated phosphate structural units are here regarded as borophosphates as well, although they actually have to be classified as borate−phosphates. But this distinction is not pursued any further.

Anhydrous borophosphates are listed in Table 1. Before discussing structural details it should be pointed out here that the classification "anhydrous" does not exclude hydrothermal conditions for preparation: $Sr[BPO_5]$[2,5] and $Na_5[B_2P_3O_{13}]$[6,7] are obtained under hydrothermal conditions as well as by a high-temperature route (heating of solid mixtures in open systems).

The crystal structure of α-$Zn_3[BPO_7]$[8] ($\equiv Zn_3[(BO_3)(PO_4)]$) contains isolated planar BO_3 groups and PO_4 tetrahedra. Trigonal planar borate groups sharing one common oxygen atom with a phosphate tetrahedron as well as isolated phosphate tetrahedra are present in the crystal structure of $Co_5[BP_3O_{14}]$[9] ($\equiv Co_5[(BPO_6)(PO_4)_2]$). The tetrahedral chain structures are loop-branched (formation of 3-membered rings: $M[BPO_5]$; M = Ca, Sr[2], M = Pb[10]) and open branched ($M_3[BP_3O_{12}]$; M = Ba[2], M = Pb[11]), respectively. Decreasing B:P ratios are consistent with an increasing number of PO_4 tetrahedra within the central chains (B:P = 1, pure borate chain (B chain); B:P = 0.66, BBP chain; B:P = 0.33, BP chain). The chain structures given in Table 1 show the common principle that all the corners of BO_4 tetrahedra share common corners with neighboring tetrahedra.

Hydrated borophosphates with a molar ratio B:P > 1 are given in Table 2. The chain anions contain boron in a 3-fold and in a tetrahedral coordination. BO_3 groups are exclusively linked to borate species. Terminal (nonbridging) oxygen positions of the BO_3 groups are always protonated. All the corners of BO_4 tetrahedra share common corners with neighboring units within the chains. The crystal structure of $K_3[B_5PO_{10}(OH)_3]$[12] (B:P = 5) contains a central tetrahedral borate chain which is loop-branched by single $BO_2(OH)$ and $PO_3(OH)$ groups with the sequence B···B···P along the chain. The central chains of the polymer anions in the crystal structures of $Li[B_3PO_6(OH)_3]$[13] (B:P = 3) and $(NH_4)_2[B_3PO_7(OH)_2]$[14] (B:P = 3) are built of alternating

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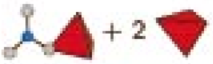
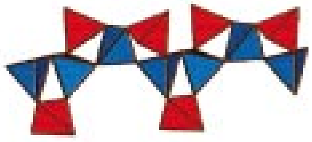
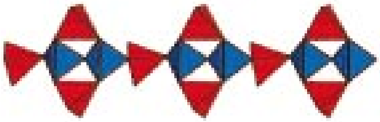
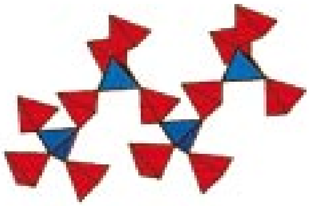
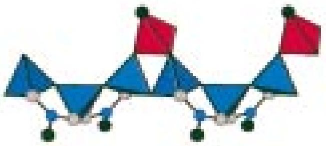
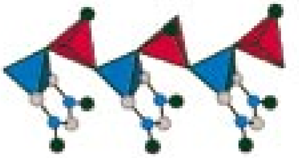
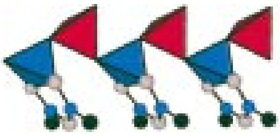
Table 1. Anhydrous Borophosphates[a]

Complex Anions	B[CN]	B:P	Compound	Ref.
single  +	[3]	1	α-$Zn_3[BPO_7]$	[8]
double/single  + 2	[3]	1 (0.33)	$Co_5[BP_3O_{14}]$	[9]
chains				
loop-branched 	[4]	1	$M[BPO_5]$ M=Ca, Sr M=Pb	[2] [10]
loop-branched 	[4]	0.66	$Na_5[B_2P_3O_{13}]$	[6]
open-branched 	[4]	0.33	$M_3[BP_3O_{12}]$ M=Ba M=Pb	[2] [11]

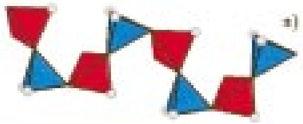
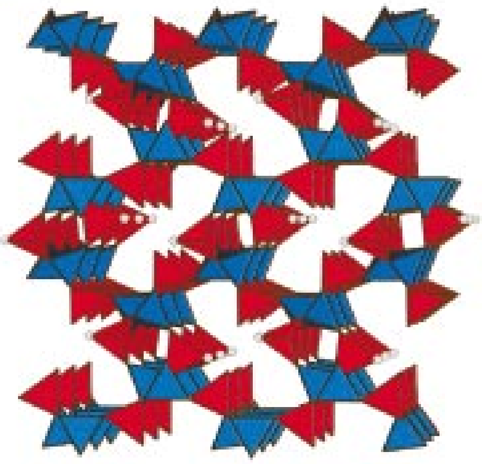
[a] Borate tetrahedra and boron atoms, blue; phosphate tetrahedra, red; oxygen atoms of BO_3 groups, gray spheres; CN = coordination number.

Table 2. Hydrated Borophosphates, B:P > 1[a]

Complex Anions	B[CN]	B:P	Compound	Ref.
chains				
loop-branched 	[3]+[4]	5	$K_3[B_5PO_{10}(OH)_3]$	[12]
open loop-branched 	[3]+[4]	3	$Li[B_3PO_6(OH)_3]$	[13]
open loop-branched 	[3]+[4]	3	$(NH_4)_2[B_3PO_7(OH)_2]$	[14]

[a] Borate tetrahedra and boron atoms, blue; phosphate tetrahedra, red; oxygen atoms at boron in trigonal planar coordination, gray spheres; OH groups, black spheres; CN = coordination number.

Table 3. Hydrated Borophosphates, B:P = 1[a]

Complex Anions	B[CN]	Compound	Ref.
single 	[4]	$Mn_3(OH)_2[B(OH)_4][PO_4]$	[15]
double 	[4]	$Mg_3(H_2O)_6[B_2(OH)_6(PO_4)_2]$	[16]
unbranched chain  *)	[4]	$Fe[B_2P_2O_7(OH)_5]$	[17]
framework  3-, 4-, 6-, 9- and 12-membered rings	[4]	$M[B_2P_2O_8(OH)]$, M=Rb, Cs	[18]

*) One of the protons of each borate tetrahedron is involved in a "symmetrical" hydrogen bridge to an adjacent chain.

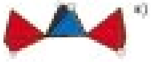
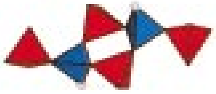
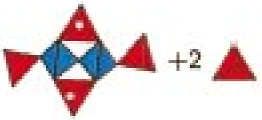
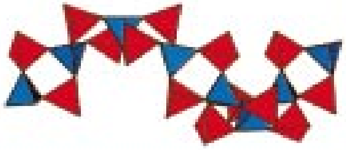
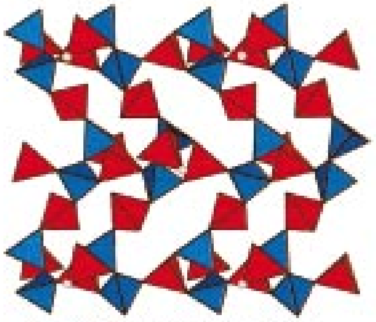
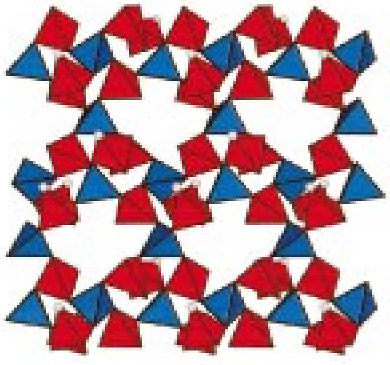
[a] Borate tetrahedra, blue; phosphate tetrahedra, red; OH groups, gray spheres; CN = coordination number.

BO_4 and $PO_3OH/(PO_4)$ groups by sharing common corners. Loop-branchings in the lithium and the ammonium compounds are restricted to single borate tetrahedra by condensation with planar dimeric units $B_2O_3(OH)_2$ and formation of 3-membered borate rings.

Hydrated borophosphates with a molar ratio B:P = 1 (Table 3) and B:P < 1 (Table 4) are exclusively built of borate and phosphate tetrahedra and do not contain boron in a trigonal planar coordination. The structures with B:P = 1 include the mineral phases seamanite ($Mn_3(OH)_2[B(OH)_4][PO_4]$)[15] and lüneburgite ($Mg_3(H_2O)_6[B_2(OH_6)(PO_4)_2]$)[16] with isolated tetrahedral units ($B(OH)_4$ and PO_4) and dimers ($(OH)_3BOPO_3$), respectively. An unbranched tetrahedral *vierer* single chain is present in the crystal structure of $Fe[B_2P_2O_7(OH)_5]$;[17] the nonbridging corners of the borate tetrahedra correspond to OH groups or are involved in "symmetrical" hydrogen bridges to adjacent polymers. The only 3-dimensional borophosphate framework known up to now is reported with the crystal structure of the isotypic compounds $M[B_2P_2O_8(OH)]$, M = Rb, Cs.[18] The complex framework consists of 3-, 4-, 6-, 9-, and 12-membered rings of tetrahedra. All the corners of the borate tetrahedra are linked to corners of neighboring borate and phosphate groups.

The phosphate-rich borophosphates (B:P < 1) are summarized in Table 4. Although the compounds are representative of "excess phosphate", no P−O−P linking is observed. The smallest tetrahedral oligomer is an unbranched triple of two phosphate groups and one borate unit sharing common corners ($NaFe[BP_2O_7OH)_3]$[19] and $Mg_2[BP_2O_7(OH)_3]$[20]). The condensation of two unbranched tetrahedral triples leads to an open-branched 4-membered ring ($K_2Fe_2[B_2P_4O_{16}(OH)_2]$)[19] and to a loop-branched chain fragment ($Na_4Cu_3[B_2P_4O_{15}(OH)_2]\cdot 2HPO_4$),[21] respectively. The sodium−copper compound

Table 4. Hydrated Borophosphates, B:P < 1[a]

Complex Anions	B[CN]	B:P	Compound	Ref.
oligomers				
unbranched triple 	[4]	0.5	$NaFe[BP_2O_7(OH)_3]$	[19]
open-branched ring 	[4]	0.5	$K_2Fe_2[B_2P_4O_{16}(OH)_2]$	[19]
loop-branched + single 	[4]	0.5 (0.33)	$Na_4Cu_3[B_2P_4O_{15}(OH)_2]\cdot 2HPO_4$	[18]
loop-branched chain 	[4]	0.5	$M^IM^{II}(H_2O)_2[BP_2O_8]\cdot H_2O$, M^I=Na, K; M^{II}=Mg, Mn, Fe, Co, Ni, Zn	[22]
layers  3- and 9-membered rings	[4]	0.66	$Co(C_2N_2H_{10})[B_2P_3O_{12}(OH)]$	[23]
 6- and 8-membered rings	[4]	0.5	$Na_{1.89}Ag_{0.11}[BP_2O_7(OH)]$ $Na_2[BP_2O_7(OH)]$	[24]

*) Protons of the phosphate tetrahedra are involved in a "symmetrical" hydrogen bridge to adjacent oligomers.

[a] Borate tetrahedra, blue; phosphate tetrahedra, red; OH groups, gray spheres; CN = coordination number.

additionally contains isolated HPO_4 groups. The isotypic compounds $M^IM^{II}(H_2O)_2[BP_2O_8]\cdot H_2O$ (M^I = Na, K; M^{II} = Mg, Mn, Fe, Co, Ni, Cu)[22] contain infinite 6_1-helices from loop-branched tetrahedral chains. The central chain is built of alternating borate and phosphate units; linking of two borate tetrahedra by an additional PO_4 group along the chain leads to the formation of 4-membered tetrahedral rings. The class of borophosphates with B:P < 1 also includes the tetrahedral layer structures $Co(C_2N_2H_{10})[B_2P_3O_{12}(OH)]$[23]

and $Na_2[BP_2O_7(OH)]/Na_{1.89}Ag_{0.11}[BP_2O_7(OH)]$,[24] which consist of 3- and 9-, and 6- and 8-membered rings, respectively. In agreement with the peculiarity of the framework structure $M[B_2P_2O_8(OH)]$,[18] tertiary phosphate tetrahedra are also present in the layer structures.

Although the definite number of crystal structures of borophosphates known up to now is rather small, a first approach to a structural chemistry of borophosphates is proposed in the present paper. On the basis of the structural classifications summarized in Tables 1−4 the following supplementary principles should be pointed out in conclusion:

(1) Compounds with a molar ratio B:P > 1 contain boron in 3-fold and tetrahedral coordination.

(2) Nonbridging corners of borate species in hydrated phases correspond to OH groups.

(3) Analogies to the structural chemistry of borates[25] are also given by the frequent formation of 3-membered rings.

(4) P−O−P linking is not observed.

(5) Relations to the structural chemistry of phosphates[26] are given by the presence of tertiary phosphate tetrahedra (see ultraphosphates) in layer and framework structures.

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