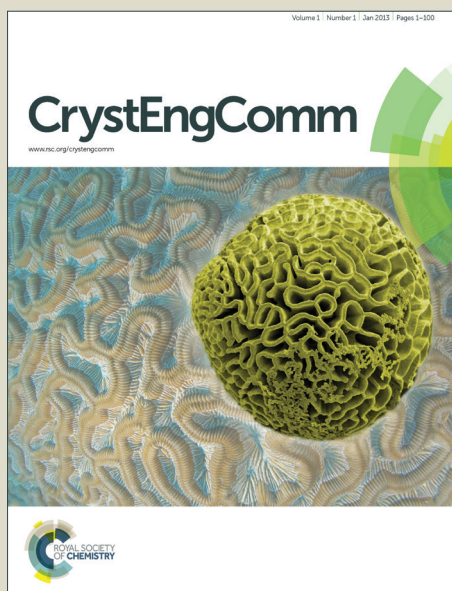


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COMMUNICATION

K₇B₂P₅O₁₉: A Novel Alkali Metal Borophosphate with Zero Dimensional [B₂P₅O₁₉]⁷⁻ Anionic Units†

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A new anhydrous alkali metal borophosphate K₇B₂P₅O₁₉, which exhibits a novel zero dimensional [B₂P₅O₁₉]⁷⁻ anionic unit with internal connected P-O-P bonds, has been successfully synthesized and structurally characterized.

The structural chemistry of borophosphate is dominated by the anionic partial structures constructed by BO₃, BO₄ or PO₄ groups via sharing common corners. The great number of different possibilities for the connection mode among BO₃ triangles, BO₄ or PO₄ tetrahedra leads to the large group of borophosphates with new connection patterns and variable extension of the anionic partial structures.¹ The structural versatility of borophosphates gives rise for special properties of this class of compounds and many of them are potential functional materials.² Therefore, it is of great interest to perform structural investigations as well as chemical modifications on borophosphates. The fundamental building units (FBUs) and the B/P ratio are two important classification criteria of borophosphates.³ On the one hand, complex anionic partial structures of borophosphates can be simply disassembled into their FBUs. On the other hand, different B/P ratio of FBUs can lead to diverse dimensionality of the anionic partial structures, ranging from clusters, chains, to layers and frameworks.

According to literatures, FBUs with different structural patterns and different B/P ratios are summarized.^{3a, 3b} Although many different FBUs have been described, a linking of PO₄ tetrahedra, that is, the formation of P-O-P bonds is rare in borophosphates. The absence of P-O-P connections in typical borophosphates could be explained by Pauling's fourth rule.⁴ Not until 2010, P-O-P connections have never been found in the crystal structures of borophosphates.⁵ Recently, we have offered further examples containing P-O-P connections: Li₂Cs₂B₂P₄O₁₅ and Li₃M₂BP₄O₁₄ (M=K, Rb).⁶ Those compounds are all mixed-metal MM' borophosphates (M and M' are two different metal cation). In general, by increasing phosphate content in borophosphates (lower the B/P ratio in FBUs), there would be more phosphate groups occupying terminal positions so that the dimensionality of anionic partial structures decreases and even isolated phosphate groups appear.^{3a} However, when P-O-P bonds occur, terminal PO₄ tetrahedra can further condensate into polyanionic groups and the

dimensionality of anionic partial structures will not strongly depend on B/P ratio. Herein, the existence of the P-O-P connection has largely extended the chemical diversity of borophosphates. Considering the dimensionality of those compounds containing P-O-P connections, one may find that anionic partial structures with one dimensional (1D) chains, two dimensional (2D) layers, three dimensional (3D) frameworks, have been reported,⁵⁻⁶ however, zero dimensional (0D) clusters or oligomers were never observed. In the present study, a new anhydrous alkali metal borophosphate, K₇B₂P₅O₁₉ has been synthesized. Interestingly, the structure of this compound contains a unique 0D FBU with internal connected P-O-P bonds. Here we report the synthesis and characterization of this compound.

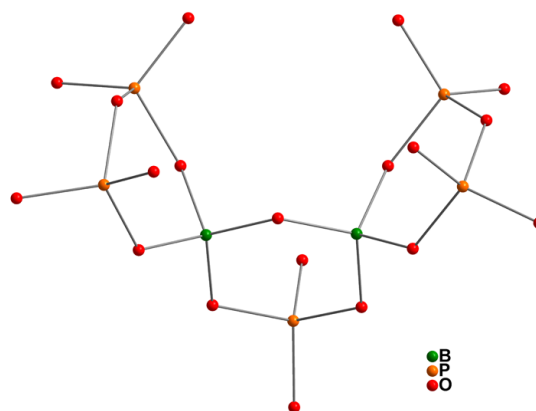


Figure 1. View of the structures of 0D [B₂P₅O₁₉]⁷⁻ unit in K₇B₂P₅O₁₉.

The title compound was synthesized by spontaneous crystallization. Because borates and phosphates are known to be glass forming materials, it is difficult to prepare crystalline phase from the high-temperature solution of K₂O - B₂O₃ - P₂O₅ system. In order to reduce the viscosity, KCl was introduced as the flux. The whole structure of K₇B₂P₅O₁₉ (triclinic, *P*1̄) could be described as a complicated 3D framework composed of 0D [B₂P₅O₁₉]⁷⁻ anionic

units and KO_n ($n = 6 \sim 10$) distorted polyhedra. One of the novel features in $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ is the 0D $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ anionic unit, consisting of three six-membered rings in which two BO_4 tetrahedra and five PO_4 tetrahedra are linked by vertical oxygen atoms (Figure 1). This unit could be recognized as the FBU of $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$, and it can also be described as the combination of two (BP_2O_7) and one ($\text{B}_2\text{P}_2\text{O}_7$) six-membered rings. The dihedral angles between two (BP_2O_7) and central ($\text{B}_2\text{P}_2\text{O}_7$) least-squares ring planes are 79.57° and 86.97° , respectively. In this unit, all B and P atoms are tetrahedrally coordinated with B-O distances varying in the range of 1.420(5)–1.511(4) Å and P-O distances ranging from 1.462(3) to 1.632(3) Å, respectively. The O-B-O and O-P-O angles are in the ranges $106.2(3)$ – $113.5(3)^\circ$ and $102.16(1)$ – $118.10(1)^\circ$, respectively. The deviations of the BO_4 and PO_4 tetrahedra from the ideal symmetry can be measured by the method suggested by Balic-Zunic and Makovicky.⁷ In $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$, the calculated values of deviations are all less than 0.5 % (BO_4 : 0.11–0.13 %, PO_4 : 0.04–0.31 %) and therefore, all of the tetrahedra may be classified as regular.

According to the classification of FBUs in borophosphate proposed by Kniep et al.,^{3a} the shorthand descriptor of $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ unit is $7\Box: <3\Box>-<3\Box>-<3\Box>$ (in which symbol $\Box$ represents BO_4 and PO_4 tetrahedra). It is noted that the number of borophosphates with a B/P ratio = 2:5 is small. As far as we know, such a $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ FBU has never been found in borophosphates. In comparison, a similar FBU, $[\text{B}_2\text{P}_5\text{O}_{16}(\text{OH})_5]^{6-}$ (represented as $7\Box: <3\Box>|\Box|\Box|\Box|\Box|$, Figure 2a) was found in the crystal structure of $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{VB}_2\text{P}_5\text{O}_{17}(\text{OH})_5] \cdot \text{H}_2\text{O} \cdot \text{H}_3\text{PO}_4$.⁸ The difference is that the terminal PO_4 tetrahedra of $[\text{B}_2\text{P}_5\text{O}_{16}(\text{OH})_5]^{6-}$ unit are not internal connected but linked with VO_5 unit forming a $[\text{V}^{\text{IV}}\text{OB}_2\text{P}_5\text{O}_{16}(\text{OH})_5]^{4-}$ heteropolyoxoanion cluster. Moreover, the $[\text{B}_7\text{O}_{14}]^{7-}$ heptaborate unit, observed in the structures of $\text{Li}_4\text{Cs}_3\text{B}_7\text{O}_{14}$ ⁹ and $\text{KBa}_7\text{Mg}_2\text{B}_{14}\text{O}_{28}\text{F}_5$,¹⁰ could be viewed as the prototype for the $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ unit. As seen from Figure 2b, the five BO_3 triangles in $[\text{B}_7\text{O}_{14}]^{7-}$ are substituted by five PO_4 tetrahedra leading to the formation of $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ unit. It is noted that the $[\text{B}_7\text{O}_{14}]^{7-}$ units in $\text{Li}_4\text{Cs}_3\text{B}_7\text{O}_{14}$ and $\text{KBa}_7\text{Mg}_2\text{B}_{14}\text{O}_{28}\text{F}_5$ are isolated, that is to say, they are also 0D anionic clusters.

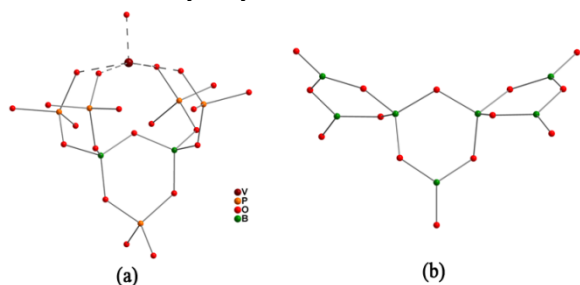


Figure 2. View of the structures of (a) $[\text{B}_2\text{P}_5\text{O}_{16}(\text{OH})_5]^{6-}$ unit (H atoms are omitted); (b) $[\text{B}_7\text{O}_{14}]^{7-}$ unit.

Of particular interest is that $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ contains the unusually corner-shared PO_4 tetrahedra, namely, the direct P-O-P connections in $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ unit. The IR spectrum for $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ displays absorption peaks around 1134 and 1035 cm^{-1} , which are attributed to the characteristic absorption of P-O-P bonds (Figure. S1 in the ESI†).^{6, 11} Up to now, there are four different kinds of FBUs with P-O-P connections in borophosphates: $[\text{B}_4\text{P}_8\text{O}_{30}]^{8-}$ unit with B:P = 1:2,⁶ $[\text{B}(\text{PO}_4)(\text{P}_2\text{O}_7)]^{4-}$ unit with B:P = 1:3,⁵ $[\text{B}(\text{P}_2\text{O}_7)_2]^{5-}$ unit with B:P = 1:4,^{5, 6} and $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ unit described here with B:P = 2:5 (Figure. S2 in the ESI†). In these FBUs, boron and phosphorus atoms are all in tetrahedral coordination, and B:P < 1 is satisfied in order to form additional P-O-P bonds. In addition, the P-O bonds with the longest bond length are always those involved in the P-O-P connections. In the view of connectivity, the $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ unit is an isolated FBU with internal connected P-O-P bonds, whereas other

three kinds of FBUs are further connected by either P-O-P or B-O-P bonds forming chains, layers and frameworks (Table S3 in the ESI†). Therefore, in this communication, we demonstrate the first example of 0D $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ anionic units with P-O-P bonds in borophosphates.

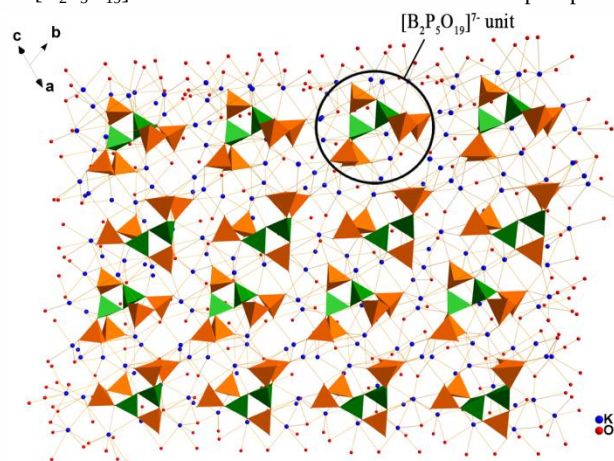


Figure 3. View of the arrangement of 0D $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ anionic units along $[101]$ direction (BO_4 tetrahedra: green; PO_4 tetrahedra: yellow).

In $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$, there are eight different KO_n ($n = 6 \sim 10$) distorted polyhedra with K-O bond lengths ranging from 2.582(3) to 3.234(2) Å (average distance 2.911 Å). The K(8) site is only half occupied (see experimental section). Figure 3 shows the arrangement of $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ FBUs along $[101]$ direction. All the KO_n polyhedra are connected with $[\text{B}_2\text{P}_5\text{O}_{19}]^{7-}$ FBUs to form a 3D framework. The bond valence sums (BVS) for all atoms in $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ are calculated.¹² These values are comparable with the valences of the elements (Table S1 in the ESI†). In addition, we checked our structure model for electrostatic reasonability by Madelung energy calculations using the VESTA program.¹³ Because of the additive potential of the Madelung energy, it is possible to calculate hypothetical values starting from the binary oxides. As presented in Table 1, the value of the Madelung energy for $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ calculated with the structure parameters was almost identical to the sum of calculated values of the binary components, and therefore, the structure model of $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ shows electrostatic consistency.

Table 1. Results of the Madelung energy calculation for $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ compared with the sum of calculated values of the binary components.

$\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$	$7/2 \text{ K}_2\text{O}^{14} + \text{B}_2\text{O}_3^{15} + 5/2 \text{ P}_2\text{O}_5^{16}$
Madelung energy = -143071 kJ/mol ($\Delta = 0.22\%$)	Madelung energy = -143386 kJ/mol

The preparation of $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ polycrystalline samples was attempted via conventional solid-state reactions. At first, the polycrystalline samples were synthesized using stoichiometric mixture of K_2CO_3 , H_3BO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$. The mixture was heated in air between $450 - 650^\circ\text{C}$. However, pure phase of $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$ was difficult to obtain, and only KPO_3 (PDF No. 35-0819) and some undetermined amorphous were revealed by powder X-ray diffraction (XRD) studies. Then, polycrystalline samples were prepared by using stoichiometric mixture of $\text{K}_4\text{P}_2\text{O}_7$, KH_2PO_4 and H_3BO_3 as starting materials. The mixture was calcined in air at 550°C for 1 week with several intermediate grindings until single phase was obtained. The purity of sample was confirmed by powder XRD studies (Figure S3 in the ESI†). Considering the uncommon P-O-P connection in $\text{K}_7\text{B}_2\text{P}_5\text{O}_{19}$, it seems that the raw materials containing

similar P-O-P connection, such as pyrophosphates, might be a better choice for the synthesis of pure phase.

The thermal behavior of $K_7B_2P_5O_{19}$ was measured ranging from 50 to 900 °C (Figure S4 in the ESI†). This compound is thermally stable up to 650 °C (melting point proven by heating experiment). No weight loss is observed in whole temperature range. Although many borophosphates could be prepared either by conventional hydrothermal/solvothermal method or recent developed ionothermal method, all reported compounds containing P-O-P connections are anhydrous ones, which are synthesized by solid-state method or flux method, and show good thermal stability. The UV-Vis-NIR diffuse reflectance spectrum measurements on powder samples of $K_7B_2P_5O_{19}$ exhibit no absorption in the range from 190 to 2600 nm, and the band gap of $K_7B_2P_5O_{19}$ is about 5.46 eV (Figure S5 in the ESI†). It is clear that this compound has a short UV cut-off edge, and can be used as a UV optical material.

Electronic structure calculations were performed in order to examine the band structures as well as to better understand relation between electronic structures and optical properties. The calculated band structures of $K_7B_2P_5O_{19}$ along high symmetry points of the first Brillouin zone are plotted in Figure S6 in the ESI†. It is found that the highest energy of the valence bands (VBs) and the lowest of the conduction bands (CBs) are both localized at the G point with a direct band gap of 4.75 eV, which is close to the experimental value. The bands can be assigned according to the total and partial densities of states as plotted in Figure S7 in the ESI†. For $K_7B_2P_5O_{19}$, the band structures can be divided into two principal groups separated by the energy gap. The VBs close to Fermi energy (E_F) are mainly due to the contributions of 2p orbitals of oxygen atoms. The CBs are primarily from the 3p hybridization orbitals of K and P atoms. Therefore, the absorption spectra of $K_7B_2P_5O_{19}$ can be explained as charge transfers from the O 2p orbitals to the 3p hybridization orbitals of K and P atoms.

In summary, a new alkali metal borophosphate, $K_7B_2P_5O_{19}$ has been synthesized and characterized. It has a 3D framework that is built up of KO_n ($n = 6 \sim 10$) distorted polyhedra and the $0D [B_2P_5O_{19}]^{7-}$ anionic units. To the best of our knowledge, this $[B_2P_5O_{19}]^{7-}$ FBU with direct P-O-P bonds is found for the first time in borophosphates. It will complement the borophosphate chemistry. Detailed investigations on the physical properties of $K_7B_2P_5O_{19}$ are in progress.

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Notes and references

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† Single crystals of $K_7B_2P_5O_{19}$ were obtained from a mixture of KCl, H_3BO_3 and $NH_4H_2PO_4$ in the molar ratio of 1:1:2 by the high temperature solution method. The mixture (10 g) was kept at 700 °C for 24 h in a programmable-temperature electric furnace. The homogenized solution was slowly cooled to 500 °C at a rate of 3 °C/h, and finally cooled to RT at a rate of 50 °C/h. The crystal structure was determined by single-crystal XRD on an APEX II CCD diffractometer using monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 296(2) K and integrated with the SAINT program.¹⁷ The numerical absorption corrections were carried out using the SCALE program for area detector. All calculations were performed with programs from the SHELXTL crystallographic software package.¹⁸ The structure was solved by direct methods with space group $P\bar{1}$. During the refinement, the K(8) site was found to exhibit large displacement parameter, and the formula was charge unbalance. In addition, in order to rule out the possibility of lower space group $P1$, the sample was irradiated with 1064 nm Nd:YAG laser beam, and there was no second harmonic generation signal (532 nm, green light). Therefore, the assignment of centrosymmetric space group was reasonable, and K(8) atom was refined as a partially occupied site. The final site occupancy factor of K(8) atom was refined to 0.496. All atoms were refined using full matrix least-squares techniques with isotropic thermal parameters, and final least-squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structure was checked for missing symmetry elements with PLATON.¹⁹ Crystal data (CCDC: 995146): Triclinic, space group $P\bar{1}$, $a = 9.9795(8)$ Å, $b = 10.1903(8)$ Å, $c = 11.6966(9)$ Å, $\alpha = 91.086(5)^\circ$, $\beta = 101.528(5)^\circ$, $\gamma = 118.691(4)^\circ$, $V = 1013.21(14)$ Å³, $Z = 2$, $D_c = 2.472$ g/cm³, $\mu = 1.980$ mm⁻¹, $F(000) = 740$, $GOF = 1.111$, $R_1 = 0.0401$ and $wR_2 = 0.0939$ ($F_o^2 \geq 2\sigma(F_o^2)$).

Electronic Supplementary Information (ESI) available: X-ray data in CIF format, atomic coordinates and equivalent isotropic displacement parameters, selected bond distances and angles, comparison of FBUs with P-O-P connections, diagrams of powder XRD and thermal measurements, IR and UV-Vis-NIR diffuse-reflectance spectra. See DOI: 10.1039/c000000x/

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Tables of Contents

K₇B₂P₅O₁₉: A Novel Alkali Metal Borophosphate with Zero Dimensional [B₂P₅O₁₉]⁷⁻ Anionic Units

Ying Wang, Shilie Pan, Shujuan Han, Bingbing Zhang, Lingyun Dong, Min Zhang and Zhihua Yang

K₇B₂P₅O₁₉ exhibits a novel zero dimensional [B₂P₅O₁₉]⁷⁻ anionic unit with internal connected P-O-P bonds.

