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Ionothermal Syntheses and Characterizations of New Open-Framework Metal Borophosphates

Tan Su,[†] Hongzhu Xing,[‡] Jin Xu,[†] Jihong Yu,*[,†] and Ruren Xu[†]

[†] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China, and* [‡] *College of Chemistry, Northeast Normal University, Changchun 130024, P. R. China*

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Three new open-framework metal borophosphates, $[Na_6Co_3B_2P_5O_{21}Cl]\cdot H_2O$ (JIS-4), $K_5Mn_2B_2P_5O_{19}(OH)_2$ (JIS-5), $(NH_4)_8[Co_2B_4P_8O_{30}(OH)_4]$ (JIS-6), have been prepared under ionothermal conditions using ionic liquid 1-ethyl-3-methylimidazolium ([Emim]Br) as the solvent. They are the first examples of metalloborophosphate prepared by the ionothermal method. Their structures are determined by single-crystal X-ray diffraction. The 3-D open framework of JIS-4 is made of CoO_5Cl octahedra, CoO_5 square pyramids, and PO_4 and BO_4 tetrahedra forming 12-ring channels along the [010] direction. It is noted that JIS-4 is the first 3-D open-framework structure in the family of borophosphate with the B/P ratio of 2/5, which features a borophosphate cluster anionic partial structure. Such cluster anionic partial structures connect with MnO_6 octahedra and MnO_5 trigonal bipyramids resulting in the formation of the 2-D layer structure of JIS-5 with the same B/P ratio as JIS-4. The 2-D layer structure of JIS-6 belongs to the largest family of borophosphate with a B/P ratio of 1/2 which features a unique 1-D chain anionic partial structure. Crystal data for JIS-4, orthorhombic, *Pnma*, $a = 14.0638(8)$ Å, $b = 9.8813(7)$ Å, $c = 14.0008(10)$ Å, $V = 1945.7(2)$ Å^3, and $Z = 2$; for JIS-5, monoclinic, $P2_1/n$, $a = 14.4939(3)$ Å, $b = 9.2539(3)$ Å, $c = 14.8031(4)$ Å, $\beta = 101.4600(10)°$, $V = 1945.88(9)$ Å^3, and $Z = 4$. For JIS-6, triclinic, $P1$, $a = 9.6928(3)$ Å, $b = 9.8747(3)$ Å, $c = 10.0125(2)$ Å, $\alpha = 62.057(2)°$, $\beta = 82.456(2)°$, $\gamma = 76.095(2)°$, $V = 821.60(4)$ Å^3, and $Z = 1$.

Introduction

Inorganic open-framework compounds are of immense interest in chemistry and materials science because of their applications as catalysts, ion-exchangers, or molecular sieves.[1-6] Extensive research has focused on the open-framework metal borophosphates in recent years owing to their diverse structural architectures and interesting properties in optics and electrooptics.[7,8] Since the first borophosphate, $(C_2H_{10}N_2)[CoB_2P_3O_{12}(OH)]$, with an open framework structure was reported in 1996,[9] a broad spectrum of borophosphates with various dimensionalities and stoichiometries have been prepared using hydro-/solvothermal and boric acid flux methods with or without organic amines as templates.[10-15] The structural chemistry of borophosphates features diverse B/P ratios and various anionic partial structures (containing only boron and phosphorus polyhedra) such as oligomeric units, chains, ribbons, layers, and 3-D frameworks.[7,10] However, it is worth noting that, in the family of open-framework borophosphates, compounds with B/P ratio of 2/5 comprises only two reported structures.[8] The 3-D framework anionic partial structures are rarely reported.[16-18] Besides the various anionic partial structures, transition metal ions play important roles in the formation of

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*To whom correspondence should be addressed. E-mail: jihong@jlu.edu.cn. Fax: +86-431-85168608. Tel: +86-431-85168608.

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borophosphate structures and show rich diversity of the coordination geometries and coordination environments. It is interesting to observe a pentacoordinated square pyramid for vanadium[10,19] and copper ions.[20] Considering the framework elements, two chlorine substituted compounds, $(C_6H_{14}N_2)\{Zn[ZnB_2P_4O_{15}(OH)_2]\cdot(C_6H_{13}N_2)Cl\}$[21] and $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$,[22] have been reported where the chlorine ligands instead of oxygen are observed in the coordination sphere of zinc and cadmium ions, respectively. It is noted that, up to date, even for the whole family of borophosphates, only a small number of compounds are known in which the oxoligands of the complex anions are substituted.[23,24]

Open-framework materials are typically synthesized using hydro-/solvothermal methods. Recent research has revealed that the ionothermal synthesis,[25,26] i.e., the use of ionic liquid as solvent and sometimes template or structure-directing agent, is a promising technique in preparing inorganic open frameworks with novel structures and special properties, which are difficult to obtain by routine hydro-/solvothermal methods.[27−29] Ionothermal synthesis is currently receiving great attention by chemists because of the different chemistry of ionic liquid solvent system compared to that of the traditionally used water/alcohols in hydro-/solvothermal conditions. Many more open-framework compounds with new structural architectures, new compositions, and interesting properties have been prepared by ionothermal method. Very recently, we reported the ionothermal synthesis of an open-framework nickel phosphite (JIS-3) with extra-large 18-ring channels and magnetic anisotropy.[30] However, ionothermal synthesis of borophosphates is rarely reported.[31−33] Considering the important role of transition metal ions played in the borophosphate system, it is expected that novel metal borophosphates with unique structure features would be prepared by the ionothermal method.

Here, we report the first ionothermal syntheses and characterizations of three new open-framework metal borophosphates, $[Na_6Co_3B_2P_5O_{21}Cl]\cdot H_2O$ (JIS-4), $K_5Mn_2B_2P_5O_{19}(OH)_2$ (JIS-5), and $(NH_4)_8[Co_2B_4P_8O_{30}(OH)_4]$ (JIS-6), using the ionic liquid 1-ethyl-3-methylimidazolium ([Emim]Br) as solvent. They all adopt new framework topologies exhibiting unique structural features unprecedented in the family of borophosphates.

Experimental Section

Synthesis and Physical Characterizations. All three compounds were prepared under ionothermal conditions using the ionic liquid 1-ethyl-3-methylimidazolium ([Emim]Br) as solvent. Other chemicals including $CoCl_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $MnCl_2\cdot 4H_2O$, H_3BO_3, $(NH_4)_2HPO_4$, $K_2HPO_4\cdot 3H_2O$, and $NaH_2PO_4\cdot 2H_2O$ were used as received in reagent grade. The mixed starting reagents were heated in 15 mL Teflon-lined autoclaves under autogenous pressure at 200 °C for several days followed by cooling to room temperature. The products were filtered off, washed with deionized water, rinsed with ethanol, purified ultrasonically, and dried in vacuum desiccators at ambient temperature.

Single-phased dark-purple crystals of $[Na_6Co_3B_2P_5O_{21}Cl]\cdot H_2O$ (JIS-4) with a yield of ~70% (based on Co) were obtained from a reaction mixture of $CoCl_2\cdot 6H_2O$ (0.238 g), NaH_2PO_4 (0.31 g), H_3BO_3 (0.062 g), and [Emim]Br (1.0 g), in a molar ratio of 1:2:1:5.24 for 10−20 days. When the amount of H_3BO_3 was increased to 2 mmol (0.124 g) in the above reaction, pink platelike crystals of $NaCoH_2BP_2O_9$[34] were obtained as a single-phase product with a yield of ~75% (based on Co). In the synthesis for $K_5Mn_2B_2P_5O_{19}(OH)_2$ (JIS-5), $MnCl_2\cdot 4H_2O$ (0.20 g), $K_2HPO_4\cdot 3H_2O$ (0.20 g), and H_3BO_3 (0.06 g) was mixed with 1.0 g [Emim]Br in a molar ratio of 1:0.9:1:5.24. Light-pink platelike crystals of JIS-5 together with a small amount of powder (about 15%) was obtained after 5 days of crystallization. It was not successful in the attempts to prepare JIS-5 analog using other alkali metal ions besides the potassium ion. As for $(NH_4)_8[Co_2B_4P_8O_{30}(OH)_4]$ (JIS-6), a mixture composed of $Co(NO_3)_2\cdot 6H_2O$ (0.29 g), $(NH_4)_2HPO_4$ (0.4 g), H_3BO_3 (0.124 g), and 1.0 g [Emim]Br with a molar ratio of 1:3:2:5.24 gave rise to the pink tetragonal-stick crystals of JIS-6 together with purple powder (about 20%). When the amount of $(NH_4)_2HPO_4$ was increased to 4 mmol (0.53 g), another platelike smaller crystalline phase was found to become a major product. However, the crystal was too small for the single-crystal data collection, and the phase was contaminated with unknown powders. All the following physical characterizations of JIS-5 and JIS-6 were based on the picked out crystals. All three compounds can also be obtained using ionic liquid 1-methyl-3-butylimidazolium bromide ([Bmim]Br) as the solvent instead of [Emim]Br.

The chemical formulas of these three compounds were primarily determined on the basis of single-crystal structure analysis. Powder X-ray diffraction (XRD) and in situ temperature dependent X-ray diffraction data were both collected on a Rigaku D-Max 2550 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) to confirm their phase identity and thermal stability, respectively. The diffraction patterns were consistent with those calculated from the structures determined by single-crystal X-ray diffraction (Figure S1, Supporting Information). The in situ temperature dependent X-ray diffraction of JIS-4 was performed at a heating rate of 10 °C min^{-1}, and the data were collected at a rate of 4°min^{-1}. Inductively coupled plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300 DV ICP instrument gave the contents of the elements in the three structures (Table S1, Supporting Information), which are consistent with the single-crystal X-ray analysis. The presence of Cl in JIS-4 was confirmed by energy-dispersive spectroscopy (EDS) analysis performed on a Hitachi, S-4300 field emission scanning electron microscope.

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Table 1. Crystal Data and Structure Refinement for $[Na_6Co_3B_2P_5O_{21}Cl]\cdot H_2O$ (JIS-4), $K_5Mn_2B_2P_5O_{19}(OH)_2$ (JIS-5), and $(NH_4)_8[Co_2B_4P_8O_{30}(OH)_4]$ (JIS-6)

	JIS-4	JIS-5	JIS-6
formula	$Na_6H_2Co_3B_2P_5O_{22}Cl$	$K_5H_2Mn_2B_2P_5O_{21}$	$N_8H_{36}Co_2B_4P_8O_{34}$
fw	880.67	817.85	1064.94
crystal system, space group	orthorhombic, *Pnma*	monoclinic, $P2_1/n$	triclinic, $P1$
a (Å)	14.0638(8)	14.4939(3)	9.6928(3)
b (Å)	9.8813(7)	9.2539(3)	9.8747(3)
c (Å)	14.0008(10)	14.8031(4)	10.0125(2)
α (deg)	90	90.00	62.057(2)
β (deg)	90	101.4600(10)	82.456(2)
γ (deg)	90	90.00	76.095(2)
V (Å^3)	1945.7(2)	1945.88(9)	821.60(4)
Z	2	4	1
D_{calcd} (g cm^{-3})	2.541	2.792	2.152
μ (mm^{-1}; Mo Kα)	4.590	2.885	1.532
$F(000)$	1411	1592	522
θ range (deg)	2.05−28.32	1.80−28.30	2.17−28.29
reflections collected	13526	13083	6042
unique data	2563	4835	4853
restraints/parameters	0/193	0/322	3/514
goodness of fit on F^{2a}	0.958	0.899	1.001
$R_1{}^b$ $[i > 2\sigma(i)]$	0.0511	0.0352	0.0523
$wR_2{}^c$ (all data)	0.1637	0.1241	0.1396

[a] Goodness-of-fit $S = [\sum w(F_o{}^2 - F_c{}^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum(w(F_o{}^2 - F_c{}^2)^2)/\sum(w(F_o{}^2)^2)]^{1/2}$.

Crystals with dimensions of 0.15 × 0.08 × 0.08 mm^3 for JIS-4, 0.1 × 0.1 × 0.09 mm^3 for JIS-5, and 0.15 × 0.08 × 0.07 mm^3 for JIS-6 were selected for data collection at 298 ± 2 K. The data were collected on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the PROCESSAUTO processing program. On the basis of systematic absences and statistics of intensity distribution, the space group was determined to be *Pnma* for JIS-4, $P2_1/n$ for JIS-5, and $P1$ for JIS-6. Direct methods were used to solve the structure using the SHELXTL crystallographic software package.[35] All framework atoms Co, Mn, B, P, Cl, and O and guest atoms K, Na, and Ow could be unambiguously located, whereas the hydrogen atoms cannot be found on the Fourier difference maps for all three compounds. The nonhydrogen atoms were refined anisotropically. The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for H atoms, converged at R_1 = 0.0511 and wR_2 = 0.1637 for JIS-4, R_1 = 0.0352 and wR_2 = 0.1241 for JIS-5, and R_1 = 0.0523 and wR_2 = 0.1396 for JIS-6. Crystallographic data are listed in Table 1, and ORTEP drawings with atomic labeling are given in the Supporting Information (Figure S2).

Thermogravimetric analyses of the three compounds, using a Perkin-Elmer TGA-7 thermogravimetric analyzer, were performed on the powder samples at a heating rate of 10 °C min^{-1} in a flow of air (Figure S3, Supporting Information). For JIS-4, a two-step mass loss of 6.1% (calcd: 6.2%, by assuming a total loss of H_2O and HCl) was observed in the TG curve. The mass loss of 4.2% at the last step mainly occurred in the temperature range of 450−650 °C and can be attributed to the loss of HCl (calcd: 4.1%), and the mass loss of 1.9% before 450 °C can be ascribed to the removal of water molecules (calcd: 2.1 wt %) in the product. The in situ temperature dependent X-ray diffraction patterns of JIS-4 show that the framework of JIS-4 is thermally stable up to 600 °C (Figure S4, Supporting Information). Both JIS-5 and JIS-6 shows mainly a one-step mass loss in a different temperature range. As indicated in the TG curve of JIS-5, a mass loss of 3.0% (calcd: 2.5%) in the range of 300−500 °C is attributed to the removal of the P−OH terminal group, whereas a total mass loss of 15.9% (calcd: 16.4%, by assuming a total loss of NH_3 and H_2O) in the range of 340−650 °C for JIS-6 can be ascribed to the decomposition of extra-framework ammonium cations and P−OH terminal groups.

Results and Discussion

JIS-4 consists of an anionic open framework $[Co_3B_2P_5O_{21}Cl]^{6-}$ which is charge balanced by sodium cations in the structure. The asymmetric unit of JIS-4 (Figure S2, Supporting Information) contains three crystallographically distinct Co atoms, three crystallographically distinct P atoms, and one crystallographically distinct B atom. The Co(1) atoms are in a distorted octahedral environment with five Co−O bonds (2.084(6)−2.117(6) Å) and a Co−Cl bond (2.591(3) Å). Both Co(2) and Co(3) atoms are in a square pyramidal coordination with the Co−O bond lengths varying in the range of 2.012(5)−2.126(5) Å. The P(1) and P(2) atoms are tetrahedrally coordinated to four oxygens shared by adjacent cobalt atoms whereas P(1) atom shares oxygens with two B atoms and two pentacoordinated Co atoms. The tetrahedrally coordinated B atom coordinates to three μ-O atoms shared by adjacent P atoms, one μ_3-O shared by both mirror related boron atoms. The B−O bond distances are in the range of 1.457(9)−1.509(8) Å.

The structure of JIS-4 is built up from the connection of CoO_5Cl octahedra, CoO_5 square pyramids, and PO_4 and BO_4 tetrahedra, giving rise to a 3D open framework. The structure features a 2D cobalt−oxygen/chloride phosphate layer containing CoO_5Cl octahedra, CoO_5 square pyramids, and PO_4 groups. The cobalt−oxygen/chloride phosphate layers perpendicular to the c axis are further connected by borate dimers to form the 3-D open framework (Figure 1a), possessing 12-ring channels along the [100] direction (Figure 1b) and 8-ring channel along the [010] direction (Figure 1c). The anionic partial structure $[B_2P_5O_{21}]^{11-}$ of JIS-4 is also the fundamental building unit (FBU), open-branched dreier-single ring heptamer (7□:[<3□>]□|□|□|□|, where □ represents tetrahedron),[8] shown in Scheme 1a. The four pendent P-centered tetrahedra in the three-membered ring of the heptamer further connect to CoO_5Cl octahedron forming cobalt-centered borophosphate cluster (Scheme 1b). The cobalt-centered clusters are further linked by different CoO_5 square pyramids (Scheme 1c) to form

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(35) Sheldrick, G. M. SHELXL, Version 5.1, Siemens Industrial Automation Inc.: Madison, WI, 1997.

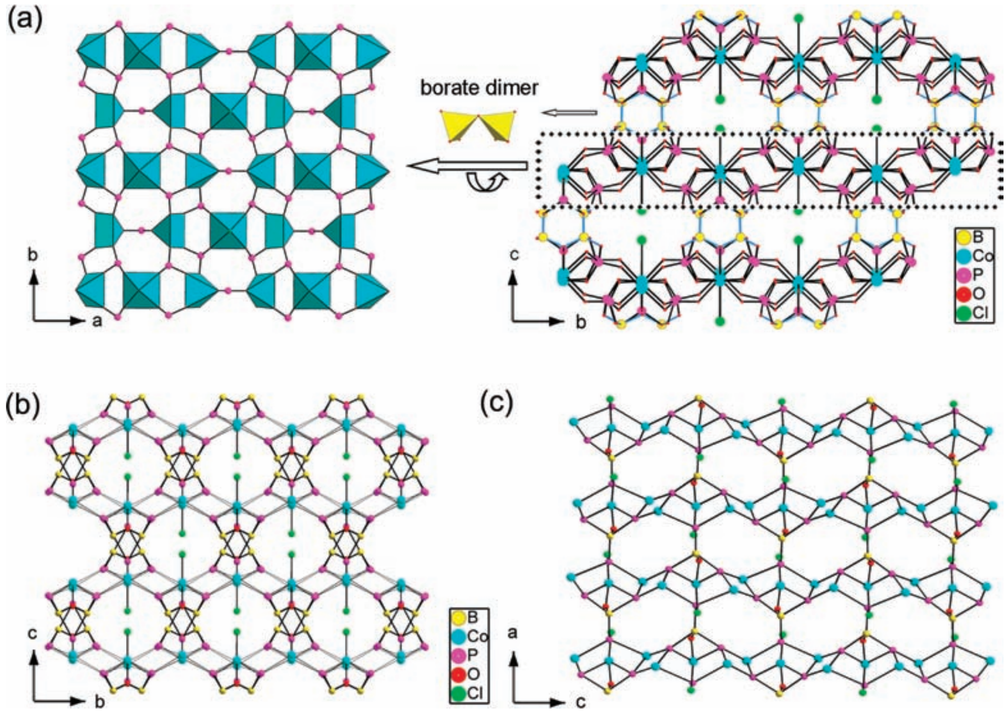
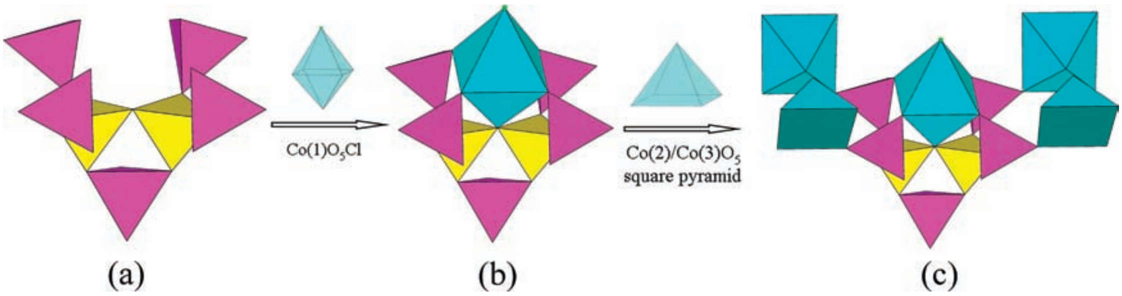


Figure 1. (a) View showing that the framework of JIS-4 consists of cobalt phosphate layers which are pillared by borate dimers. The Na atoms and H_2O molecules are ommited for clarity. (b) 12-ring channels along the [100] direction and (c) 8-ring channel along the [010] direction in the structure where the μ-O atoms, Na atoms and H_2O molecules are omitted for clarity (μ_3-O atoms are kept).

Scheme 1. How the Anionic Partial Structure and the Different Transition Metal Ions Connect in the Structure of JIS-4[a]



[a] (a) Anionic partial structure of open-branched dreier-single ring heptamer with a B/P ratio of 2/5; (b) the single Co centered borophosphate cluster; (c) the cluster is connected by square pyramids.

the 3-D framework. It is noted that, to the best of our knowledge, the square pyramidal Co ions presented in JIS-4 have not been observed in the family of open-framework borophosphates and the concomitant halide substituted coordinated metal ions are also rare.[23,24]

As mentioned above, JIS-4 can only be prepared in a narrow region with a small amount of water in the ionothermal system. At low water concentration, the strong hydrogen bonding of the water molecules in ionic liquids leads to water being less reactive than similar amounts in other solvents, which would cause the different chemistry of ionothermal condition in contrast to the routine hydro/solvothermal conditions.[36] It has been demonstrated that the amount of water presented in the ionothermal condition is important for the resultant phase. In an attempt to understand the role of water in the reaction of JIS-4, a series of experiments were designed in which the amount of water was increased gradually. It was found that JIS-4 pure phase can be obtained when less than 20 μL of deionized water (1.11×10^{-3} mmol) was added in the above reaction system, and the crystallization time would shortened correspondingly by up to 4 days. With the increase of additional water, cobalt borophosphate $NaCoH_2BP_2O_9$[34] was obtained. The results show that a small amount of water in the reaction system of JIS-4 is vital both for the crystallization rate and the phase selectivity in ionothermal synthesis, which is in accordance with the phenomena observed in the ionothermal synthesis of aluminophosphate molecular sieves. JIS-4 cannot be obtained either using H_3PO_4 as the phosphorus source or using some kinds of alcohol (e.g., ethylene glycol and n-butyl alcohol) as solvents in our experiments. We also studied the ion-exchange property of Na^+ in JIS-4, which showed no obvious ion-exchange capacity for other ions such as NH_4^+ and Li^+ ions.

JIS-5 possesses a 2-D layer structure with the same anionic partial structures $[B_2P_5O_{21}]^{11-}$ as JIS-4. The asymmetric unit of JIS-5 (Figure S2, Supporting Information) contains two

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[36] Morris, R. E. *Chem. Commun.* **2009**, 2990.

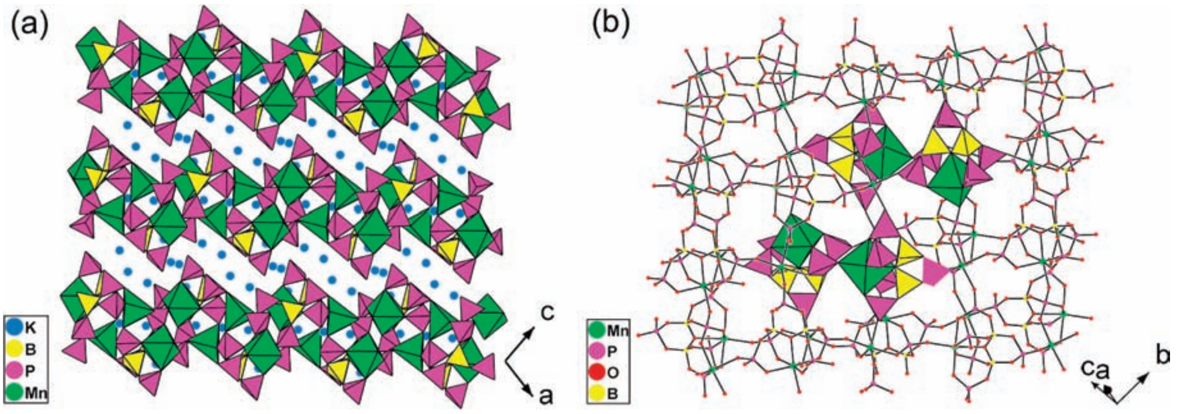

Figure 2. (a) Polyhedron view of the 2-D structure of JIS-5; the interlayer K^+ ions are presented as blue circles. (b) A layer which contains Mn centered borophosphate clusters (polyhedral). The K atoms are omitted for clarity.

crystallographically distinct Mn atoms, five crystallographically distinct P atoms, and two crystallographically distinct B atoms. The Mn(2) atom is in a distorted octahedral environment sharing five μ-O atoms with five P atoms and one μ_3-O with two boron atoms, while the Mn(1) atom in a distorted trigonal bipyramidal environment shares five bridging oxygen atoms with five P atoms. The Mn−O bond lengths vary in the range of 2.062(2)−2.268(2) Å. Five crystallographically distinct P atoms are each tetrahedrally coordinated to four oxygen atoms but in different fashions. P(1) atoms share four bridging oxygen atoms with two Mn(2) octahedra, one Mn(1) trigonal bipyramid, and one B atom. P(2) atoms share two μ-O atoms with B atoms and one μ-O atom with Mn(1) trigonal bipyramid, leaving one terminal P(2)═O(9) group with bond length of 1.497(3) Å. P(3) atoms share four bridging oxygen atoms with two Mn(1) trigonal bipyramids, one Mn(2) octahedron, and one boron atom. P(4) atom shares bridging atoms with one Mn(1), Mn(2), and B atoms, leaving one terminal P(4)═O(8) group with bond length of 1.509(3) Å, while P(5) atoms share two bridging atoms with one Mn(2) and B atoms, leaving two terminal groups of P(5)−O(1)H with bond length of 1.575(3) Å and P(5)═O(10) with bond length of 1.493(3) Å. The tetrahedrally coordinated B atom coordinates to three μ-O atoms shared by adjacent P atoms, one μ_3-O shared by both mirror related boron atoms. The B−O bond lengths range from 1.423(4) to 1.504(4) Å.

JIS-5 consists of 2-D layer anionic framework $[Mn_2B_2P_5O_{19}(OH)_2]^{5-}$ containing a distorted 8-ring in the structure (Figure 2). Potassium cations located between adjacent layers compensate the negative charge of the anionic framework. The Mn-centered borophosphate clusters (Figure 2b) similar to the Co-centered borophosphate clusters in JIS-4 can also be observed. It is interesting to note that both JIS-4 and JIS-5 possess the same B/P ratio of 2/5. Although a large number of borophosphate structures have been synthesized with various B/P ratios, up to date, the number of borophosphates with molar ratio of B/P = 2/5 is still very small with 2-D layered compound $(N_2C_3H_5)_{3.8}(H_3O)_{1.2}[(VO)_4B_2P_5O_{22}]\cdot 0.3H_2O$ (**1**) and 0-D cluster $(C_6H_{14}N_2)_2[VB_2P_5O_{17}(OH)_5]\cdot H_2O\cdot H_3PO_4$ (**2**), as known examples.[19a,37] The two vanadium borophosphates in both cases were prepared under hydrothermal conditions with organic amines as templates. Compounds **1** and **2** have two different kinds of anionic partial structure, i.e., open-branched heptamer (7□:[3□]□|□|□|□|) and open-branched dreier-single ring heptamer (7□:[<3□>]□|□|□|□|) as FBUs, respectively.[8] Both JIS-4 and JIS-5 possess the anionic partial structure $[B_2P_5O_{21}]^{11-}$ of open-branched dreier-single ring heptamer which is the same as that in compound **2**. It is worth noting that JIS-4 is the first 3D open-framework borophosphate in the family of borophosphates with B/P ratio of 2/5.

The structure of JIS-6 built up by CoO_6 octahedra and BO_4 and PO_4 tetrahedra consists of a 2-D anionic framework $[Co_2B_4P_8O_{30}(OH)_4]^{8-}$ containing 8-ring channels in the structure (Figure 3). The negative charge of the framework is compensated by the interlayer ammonium cations. The asymmetric unit (Figure S2, Supporting Information) contains two crystallographic distinct Co atoms, eight crystallographically distinct P atoms, and four crystallographically B atoms. Both of the two Co atoms are in an octahedral environment sharing five μ-O atoms with five P atoms and one μ_3-O with two boron atoms. All the crystallographically distinct P atoms are tetrahedrally coordinated to the oxygen atoms. P(1) and P(7) atom atoms are coordinated by three bridging atoms, leaving one terminal P═O group with bond length of 1.499(9) Å for P(1)═O(2) and 1.512(6) Å for P(7)═O(11), respectively. P(2), P(3), P(5), and P(6) share bridging oxygen atoms with adjacent cobalt and boron atoms, leaving one terminal P═O group (P(2)═O(9), P(3)═O(13), P(5)═O(10), and P(6)═O(22) with bond length of 1.477(9), 1.517(6), 1.512(6), and 1.509(6) Å, respectively) and one terminal P−OH group (P(2)−O(1)H, P(3)−O(3)H, P(5)−O(4)H, and P(6)−O(8)H with bond length of 1.609(10), 1.598(6), 1.577(7), and 1.593(6) Å, respectively) protruding into the interlayer void space. Both P(4) and P(8) share four bridging oxygen atoms with Co/B atoms. All the tetrahedrally coordinated B atoms coordinate to three μ-O atoms shared by adjacent P atoms and one μ_3-O shared by two mirror related boron atoms. The B−O bond lengths of 1.432(9)−1.496(9) Å are in the typical range for borophosphates.

Different from JIS-4 and JIS-5 with B/P ratio of 2/5, JIS-6 possesses 1-D open-branched dreier-single ring chain anionic partial structure $[BP_2O_{10}]^{7-}$ with B/P ratio of 1/2 (Figure 3c) as FBU. It is noted that JIS-6 has a unique anionic partial structure in contrast to the reported ones in the family of 1/2. The structure of JIS-6 can be viewed as that the 1-D FBUs connect with the transition metal Co ions resulting in the novel 2-D framework as shown in Figure 3b. It is interesting

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(37) Wistad, E.; Kritikes, M. *Acta Crystallogr.* **2003**, *c59*, 87.

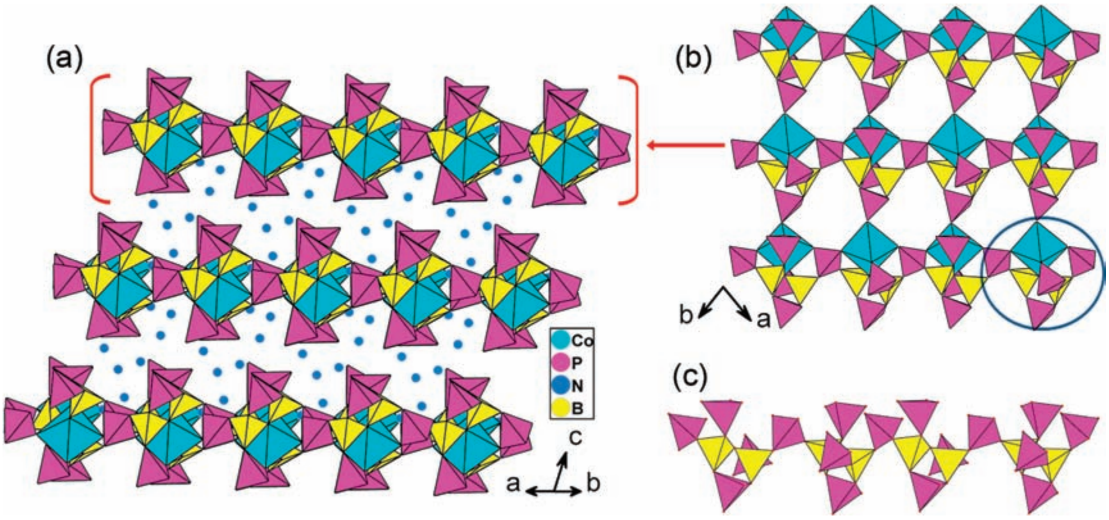

Figure 3. (a) Polyhedral view of the 2-D layered structure of JIS-6. (b) Polyhedral view of the layer containing 8-ring pore window and the Co centered borophosphate cluster is highlighted in the circle. (c) The 1-D open-branched dreier-single ring chain anionic partial structure with B/P ratio of 1/2 in the structure.

to note that JIS-6 contains similar building units, i.e., transition metal (Co) centered borophosphate heptamer, as those observed in JIS-4 and JIS-5. Such metal-centered clusters are common in the borophosphate frameworks, and even the single metal-centered borophosphate cluster compound have been reported.[37] However, JIS-4, -5, and -6 adopt three unique structures because the same borophosphate heptamers are further connected by transition metal ions in different fashions.

Conclusion

We present here the first ionothermal synthesis of three novel open-framework metal borophosphates, JIS-4, JIS-5, and JIS-6. All these structures are based on a similar cluster building unit, i.e., transition metal-centered borophosphate heptamer. The structure of JIS-4 possesses 12-ring channels along the [100] direction and 8-ring channels along the [010] direction. It is interesting to note that chlorine substituted CoO_5Cl octahedral and CoO_5 square pyramids which are rarely observed in the family of borophosphates appear in the structure of JIS-4. The 2-D layer framework of JIS-5 contains distorted 8-ring windows. It is worth noting that both JIS-4 and JIS-5 have the same anionic partial structure of open-branched dreier-single ring heptamer with B/P ratio of 2/5 and JIS-4 is the first 3-D open-framework borophosphate in the family of borophosphates with B/P ratio of 2/5. The 2-D layer structure of JIS-6 containing 8-ring pore windows possesses a 1-D chain anionic partial structure with a B/P ratio of 1/2. It is noted that JIS-6 has unique anionic partial structure in contrast to the reported ones in the family of borophosphates. The successful preparation of the three new metal borophosphates with unique structures in ionic liquids demonstrates not only that many more open-framework borophosphates with unique structures could be obtained but also that the ionothermal method is a promising method to synthesize new kinds of open-framework materials.

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Supporting Information Available: Experimental and simulated powder X-ray diffraction (XRD) patterns, in situ temperature dependent powder X-ray diffraction patterns of JIS-4, thermogravimetric curves, thermal ellipsoid plots (PDF), and X-ray crystallographic files (CIF) of the three compounds. This material is available free of charge via the Internet at http://pubs.acs.org.