

Article

A New Open-framework Iron Borophosphate from Ionic Liquids: $\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$

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Received: 11 April 2011; in revised form: 15 April 2011 / Accepted: 18 April 2011 /

Published: 19 April 2011

Abstract: A new open-framework iron borophosphate, $\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$, has been obtained by ionothermal synthesis from KH_2PO_4 , $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, H_3BO_3 and $[\text{C}_4\text{mpyr}]\text{Br}$ (1-butyl-1-methylpyrrolidinium bromide). Single-crystal X-ray diffraction analysis shows that $\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$ (monoclinic, $P2_1/c$, $a = 9.372(2) \text{ \AA}$, $b = 8.146(2) \text{ \AA}$, $c = 9.587(2) \text{ \AA}$, $\beta = 101.18(3)^\circ$, $V = 718.0(2) \text{ \AA}^3$ and $Z = 4$) has a three-dimensional (3-D) framework structure composed by $\{\text{Fe}(\text{III})\text{O}_5(\text{OH})\}$ octahedra as well as $\{\text{BO}_3(\text{OH})\}$ and $\{\text{PO}_4\}$ tetrahedra. As anionic structural sub-unit, $\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$, contains an infinite open-branched $\{[\text{BP}_2\text{O}_8(\text{OH})]^{4-}\}$ chain which is formed by alternating $\{\text{BO}_3(\text{OH})\}$ and $\{\text{PO}_4\}$ tetrahedra. $\{\text{Fe}(\text{III})\text{O}_5(\text{OH})\}$ octahedra share common O corners with five phosphate tetrahedra and the OH corner links to the hydrogen borate group to give a 3D framework. The negative charges of the inorganic framework are balanced by K^+ ions.

Keywords: iron borophosphate; ionothermal synthesis; crystal structure

1. Introduction

Open-framework iron borophosphates have received much attention for their potential magnetic properties. A broad spectrum of borophosphates with various dimensionalities and stoichiometries has been prepared using hydro-/solvothermal, as well as boric acid flux methods with or without the

employment of organic amines as templates [1-7]. So far, the ionothermal synthesis of iron borophosphates has not been explored [8-11].

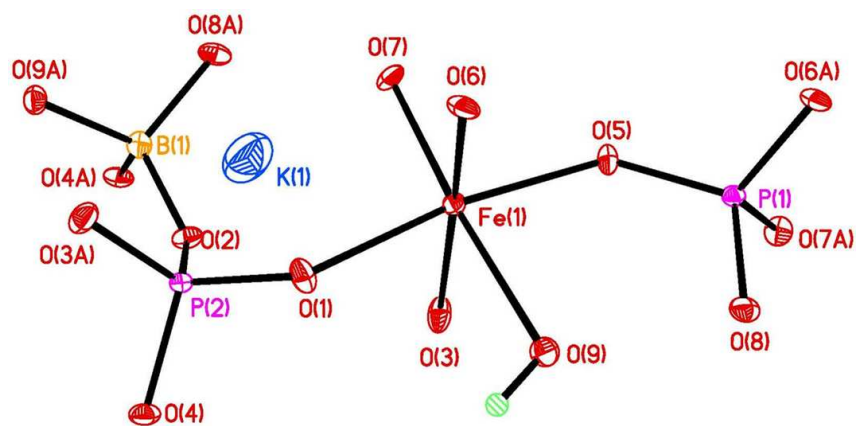
The known borophosphate anionic frameworks can be derived from a few typical borophosphate fundamental building units (FBUs) with B/P ratios of 6/1, 5/1, 3/1, 3/2, 1/1, 3/4, 2/3, 1/2, 2/5, 1/3 and 1/4 [12,13]. Among them, nonameric FBUs, $[B_3P_6X_{26}]$ [14] and $[BP_2X_8]$ [15] ($X = O, OH$) with a B/P ratio of 1/2, form the largest group. Borophosphates of the general formula $AM[BP_2O_8(OH)]$ ($A = K, Rb, Cs$ or NH_4 , $M = V, Fe, Al, Ga, Sc$) have been described in the past several years [12]. Here we report on a new member of this family, $KFe[BP_2O_8(OH)]$, obtained by ionothermal synthesis.

2. Results and Discussion

$KFe[BP_2O_8(OH)]$ was prepared by reacting ionothermally $FeCl_3 \cdot 4H_2O$, KH_2PO_4 , H_3BO_3 and 1-butyl-1-methylpyrrolidinium bromide, $[C_4mpy]Br$, in a ratio of 3:3:1;1.5 at 200 °C for 5 days. Upon cooling crystals of $KFe[BP_2O_8(OH)]$ formed. The crystal structure of $KFe[BP_2O_8(OH)]$ (monoclinic, $P2_1/c$, $a = 9.372(2)$ Å, $b = 8.146(2)$ Å, $c = 9.587(2)$ Å, $\beta = 101.18(3)^\circ$, $V = 718.0(2)$ Å³ and $Z = 4$) is built up by a 3-D framework of $\{Fe(III)O_6\}$ octahedra, $\{BO_3(OH)\}$ and $\{PO_4\}$ tetrahedra. It is isotopic with $KAl[BP_2O_8(OH)]$ [16], $(NH_4)M[BP_2O_8(OH)]$ (M, Al, Ga, Fe, V) [17-20], $RbM[BP_2O_8(OH)]$ ($M = Al, Ga, V, Fe$) [21-25], $Cs[BP_2O_8(OH)]$ ($M = Al, Ga, Fe$) [26-28].

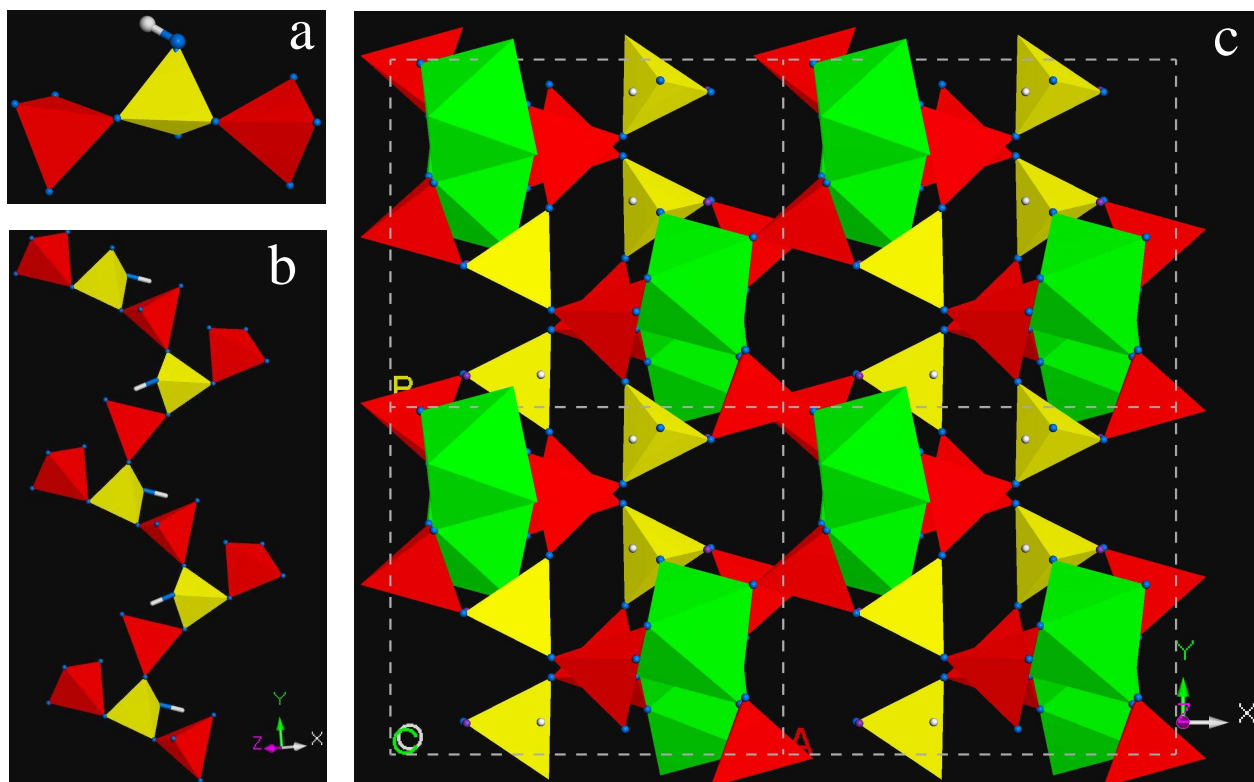
The asymmetric unit of $KFe[BP_2O_8(OH)]$ contains one crystallographically distinct Fe^{3+} cation, one B^{3+} cation, one K^+ cation, two crystallographically distinct P^{5+} cations, which are all coordinated by oxygen (Figure 1).

Figure 1. Thermal ellipsoid plot (50% probability) of the asymmetric unit of $KFe[BP_2O_8(OH)]$.



In $KFe[BP_2O_8(OH)]$, the Fe(1) atom connects three O atoms to three P(1), two O atoms to two P(2) atoms, and one O(9)H to the B(1) atom. The Fe–O internuclear distances vary in the range of 1.954(4)–2.143(4) Å. All boron and phosphorus atoms are tetrahedrally coordinated by oxygen atoms. The P(1) atom connects via three oxygen atoms to Fe(1) and one O atom to B(1) atom; the P(2) atom connects two Fe(1) atoms and two B(1) atoms via four oxygen atoms, respectively. The P–O bond lengths vary in the range of 1.505(4)–1.562(3) Å. The B(1) atom connects via one oxygen atom to a P(1) atom, two oxygen atoms to P(2) atoms and one O(9)H to Fe(1) atom, respectively. The B–O bond lengths vary in the range of 1.457(6)–1.475(7) Å.

Figure 2. **a:** Trimeric borophosphate basic building unit; **b:** open-branched vierer chain $^1_{\infty}\{[\text{BP}_2\text{O}_8(\text{OH})]^{4+}\}$ FBU; **c:** view of the open-framework structure of $\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$ along the [001] direction showing irregular 8-ring channels (color code: Fe, green; B, yellow; P, red; O, blue; K, purple; H, white).



$\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$ features an unbranched trimer, $3\text{PO}_4\text{BO}_3$, as the basic building unit (BBU) (Figure 2 a). These BBUs are connected to an infinite open-branched (oB) vierer $^1_{\infty}\{[\text{BP}_2\text{O}_8(\text{OH})]^{4+}\}$ chain (Figure 2b). The condensation of this borophosphate FBU with $\{\text{Fe}(\text{III})\text{O}_5(\text{OH})\}$ octahedra by sharing common oxygen atoms with five phosphate tetrahedra and an OH group with a hydrogenborate group link to a 3-D framework (Figure 2c). It features 8-ring channels along the [100] direction enclosed by two $\text{FeO}_5(\text{OH})$ octahedra, two $\text{BO}_3(\text{OH})$ and four PO_4 tetrahedra.

3. Experimental Section

$\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$ is prepared under ionothermal synthesis conditions using the ionic liquid 1-butyl-1-methylpyrrolidinium bromide, $[\text{C}_4\text{mpyr}]\text{Br}$, as the solvent. A mixture of $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ (99%, Fluka), KH_2PO_4 (99%, J.T. Baker), H_3BO_3 (99.8%, Appl. Chem.) and $[\text{C}_4\text{mpy}]\text{Br}$ (99%, Merck) was reacted in a 3 mL Teflon-lined stainless steel container at 200 °C for 5 days followed by cooling to room temperature. The products were filtered off, washed with deionized water and acetone, filtered by suction, and dried at 60 °C for one day.

A suitable single crystal of $\text{KFe}[\text{BP}_2\text{O}_8(\text{OH})]$ was selected for single-crystal X-ray diffraction (XRD) analysis. The data were collected at ambient temperature using graphite-monochromated Mo- $\text{K}\alpha$ radiation on an Image Plate Diffraction System, IPDS I, (Stoe, Darmstadt, Germany). The data were corrected for Lorentz and polarization effects. Data correction was carried out with the program

X-RED [29]. A face-indexed numerical absorption correction (X-SHAPE) was applied [30]. The structure was solved by direct methods and refined by full-matrix least-squares techniques with the SHELXTL crystallographic software package [31]. The Fe, B, P, and O atoms could be unambiguously located. The K^+ ions were subsequently located from a difference Fourier map. In the final refinement cycles H atoms associated with the hydroxyl groups were added computationally.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting ICSD-422900.

Crystal data for $KFe[BP_2O_8(OH)]$, ($312.71 \text{ g mol}^{-1}$); diffractometer IPDS-I, Stoe, Darmstadt; Mo- $K\alpha$ (graphite monochromator, $\lambda = 71.073 \text{ pm}$); $T = 293(2) \text{ K}$; $2\theta_{\max} = 56.18^\circ$; 100 images, $0^\circ \leq \varphi \leq 200^\circ$; $\Delta\varphi = 2^\circ$; indices: $-12 \leq h \leq 12$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$; transmission (min, max) = 0.0307, 0.0929; $\rho_{\text{calc}} = 2.893 \text{ g cm}^{-3}$; 8321 reflection intensities measured of which 1726 were symmetrically independent, $R_{\text{int}} = 0.0653$, $F(000) = 612$, $\mu = 27.547 \text{ mm}^{-1}$. Monoclinic, $P2_1/c$ (no. 62), $a = 9.372(2) \text{ \AA}$, $b = 8.146(2) \text{ \AA}$, $c = 9.587(2) \text{ \AA}$, $\beta = 101.18(3)^\circ$, $V = 718.0(2) \text{ \AA}^3$ and $Z = 4$. R values: R_1/wR_2 for final indices with $[I_o > 2\sigma(I_o)]$: 0.0400/0.1095 and for all data: 0.0541/0.1122; $S_{\text{all}} = 1.071$.

4. Conclusions

A new open-framework iron borophosphate $KFe[BP_2O_8(OH)]$, has been prepared under ionothermal conditions using the ionic liquid 1-butyl-1-methyl pyrrolidinium bromide, $[C_4\text{mpy}]Br$, as the solvent. The successful preparation of the new iron borophosphate in an ionic liquid demonstrates not only that many more open-framework borophosphates could be obtained, but also that the ionothermal method is a promising method to synthesize new kinds of open-framework materials.

Acknowledgements

This work is supported by the European Research Council (ERC) under the contract 200475.

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