

Open-framework Borophosphate: $(\text{NH}_4)_{0.5}\text{Fe}^{\text{II}}_{0.5}\text{Fe}^{\text{III}}_{0.5}\cdot(\text{H}_2\text{O})_2$ $\text{BP}_2\text{O}_8\cdot 0.5\text{H}_2\text{O}$

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Abstract: An open-framework ammonium ferricborophosphate compound was synthesized by mild hydrothermal condition at 110°C. The crystal structure has been determined by single-crystal X-ray diffraction analysis: hexagonal, $P6_322$, $a = 9.452(2)\text{ \AA}$, $c = 15.698(5)\text{ \AA}$, $\alpha = 90^\circ$, $\gamma = 120^\circ$, $Z = 6$, $M_r = 310.58$, $V = 1214.0(5)\text{ \AA}^3$, $D_c = 2.549\text{ g/cm}^3$, $\mu = 2.311\text{ mm}^{-1}$, $F(000) = 930$. The chiral tetrahedral-tetrahedral helical ribbons are linked by the mixed valance $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}\text{O}_6$ coordinated octahedra. The ammonium ions are located inside the free loop of helical ribbons close to the inner wall of the helical channels $\infty\{[\text{BP}_2\text{O}_8]^{3-}\}$, effecting on balancing charge and stabilizing helical ribbons.

Keywords: Open-framework, borophosphate, single crystal, synthesis.

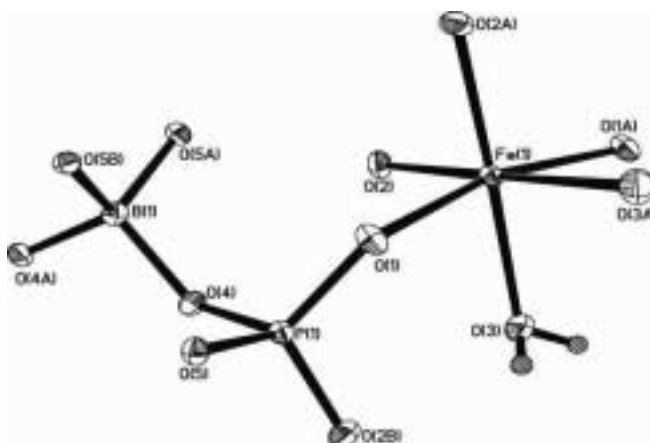
We are investigating the synthesis and properties of a new class of open framework borophosphate solids with the goal of being able to use in optical devices and magnetic materials. Only a few open-framework ferric borophosphate compounds with a chiral tetrahedra-tetrahedra helices, $\text{KFe}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8\cdot\text{H}_2\text{O}$ (**1**), $\text{Fe}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8\cdot\text{H}_2\text{O}$ (**2**), $(\text{NH}_4)_{0.4}\text{Fe}^{\text{II}}_{0.55}\text{Fe}^{\text{III}}_{0.5}(\text{H}_2\text{O})[\text{BP}_2\text{O}_8]\cdot 0.6\text{H}_2\text{O}$ (**3**) have been reported by Boy *et al.*¹, Ylmaze *et al.*² and Huang and Schäfer *et al.*³. However, Huang and Schäfer *et al.* ascertain the presence of NH_4^+ ions in the crystal structure of **2** and the replacement of octahedrally coordinated tetrameric $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ iron unit in **3** by pure FeO_6 coordination in crystal structure of **2**. Interesting in diversity of borophosphate structural chemistry, we are eager to see if any corresponding solution species are able to synthesize ferric borophosphate compounds. Truly, by adjusting experimental procedure and using different starting materials we obtained a new, open-framework ferricborophosphate compound, $(\text{NH}_4)_{0.5}\text{Fe}^{\text{II}}_{0.5}\text{Fe}^{\text{III}}_{0.5}(\text{H}_2\text{O})_2\text{BP}_2\text{O}_8\cdot 0.5\text{H}_2\text{O}$ (**IV**). In comparison with **2** and **3** aristotype structure, the mixed valance $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ existed octahedrally coordinated in crystal structure, and no five coordinates in the Fe-centered are found in **IV**. The presence of the ammonium ions stabilizes the borophosphate helical ribbons. To our knowledge is the first mixed valance ammonium ferricborophosphate. Report here is concerned the structure of a new member in ferric borophosphate family.

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Black octahedral crystals were hydrothermally obtained by reacting $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, H_3BO_3 , H_3PO_4 (85 wt %), NH_2CSNH_2 in the molar ratio of 0.5:3:1:1 and H_2O 0.25 mL in a thick wall Pyrex tube, which is frozen in liquid nitrogen, then sealed under vacuum and held at 110°C for a week. The product was filtered off, washed with water, rinsed with ether and dried at ambient temperature.

X-ray data of the crystal structure were collected on a Bruker SMART - CCD diffractometer using HELXITL program package. The isotropic displacement parameters, respectively, had a position for Fe, B, P and 4 O atoms. The mixed valance $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ was confirmed by X-ray-photoelectron spectroscopy with broad peak and the bond valence sum⁴ ($\Sigma s = 2.24$ for Fe^{2+} and $\Sigma s = 2.4$ for Fe^{3+}). 2.69 % nitrogen elements inspected by elemental analysis was confirmed by IR spectrum which displayed a characteritic N-H deformation vibration at 1436 cm^{-1} , 3272 cm^{-1} . The thermal properties were further investigated to show three steps with a total mass lose of 18% (calcd 17%). The first and second stages, being not obviously distinguished, were lost of 2.5 mol water molecules. The release of NH_3 at final stage at 600°C indicates the presence of the ammonium ions. The isotropic displacement parameters for O(6) and O(6') were refined together. Because the two oxygen positions O(6) and O(6') were only $0.77(4)\text{ \AA}$, oxygen atoms were considered to be disordered in these two positions, and assigned to oxygen and nitrogen positions. The sum of their occupancies was constrained to unity. The charge balancing cations was 0.5 mole NH_4^+ from electroneutrality.

Figure 1 ORTEP coordinated environment for view of Fe, P, and B atoms in asymmetric unit



The title compound crystallized in space group $P6_322$, with lattice parameters $a = 9.452(2)\text{ \AA}$, $c = 15.698(5)\text{ \AA}$, $\alpha = 90^\circ$, $\gamma = 120^\circ$, $Z = 6$. View of the framework atom asymmetric unit was given in **Figure 1**. Both Fe and B atoms located on the crystallographic 2-fold axis that was aligned along the unit cell c axis, respectively, octahedrally and tetrahedrally coordinated to adjacent oxygen atoms with $d_{\text{av}}(\text{Fe-O}) = 2.103\text{ \AA}$ and $d(\text{B-O}) = 1.469\text{ \AA}$. The tetrahedral phosphorus atom, with $d_{\text{av}}(\text{P-O}) = 1.526\text{ \AA}$, bonded to Fe atom and B atom *via* oxygen-atom bridges. The four framework

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oxygen atoms, O(1), O(2), O(4) and O(5) partake in Fe-O-P($\theta_{\text{av}} = 135.85$) and P-O-B($\theta_{\text{av}} = 129.30$) linked. The third oxygen atom O(3) was coordinated to the iron and because of the 2-fold symmetry on the iron atom, each iron actually bonded to two O(3) atoms, making iron octahedrally coordinated. The distance Fe^{II}/Fe^{III} to the terminal H₂O ligands was 2.191 Å. The Fe^{II}/Fe^{III}O₆ octahedra showed the distorted corresponding to the longest distance from Fe center to *cis*-positioned two terminal oxygen. There was not iron tetrameric unit in crystal structure of **IV**. The compound was isostructural with **3**, but the noticeable difference in bond distance caused by Fe^{II}/Fe^{III}O₄(H₂O)₂ **IV** and tetrameric Fe^{III}O₂(H₂O)₃ / [Fe^{III}O₄(H₂O)₂]₃ **3** coordinated in different form. The shorter P-O distance $d_{\text{av}} = 1.526$ Å, compared to P-O $d_{\text{av}} = 1.536$ Å affected the geometry of the connecting BO₄ tetrahedra, ideal and the deformed in (**IV**) and (**3**), respectively. Also, the Fe-O_{H₂O} distance was obviously shorter $d = 2.191$ Å than $d_{\text{av}} = 2.23$ Å in **IV** and **3**.

Figure 2 Polyhedral connectivity of BO₄ and PO₄ tetrahedral helix

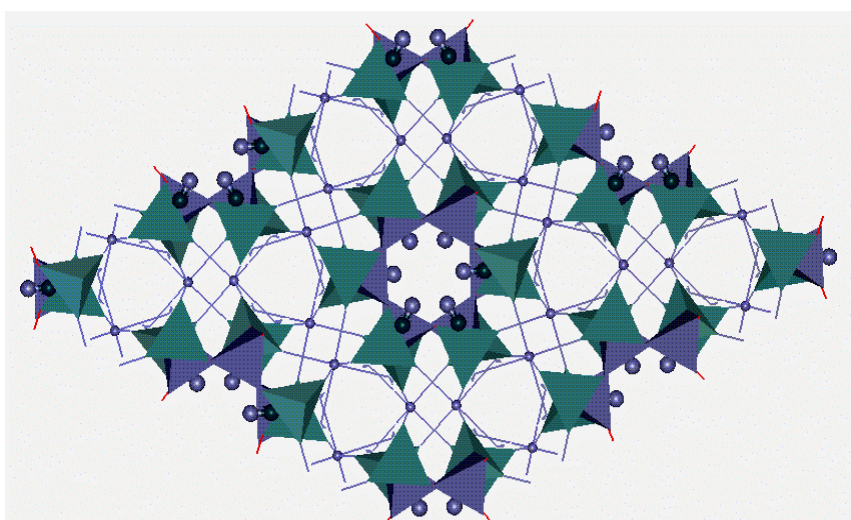


That the anionic partial structure was a condensation of PO₄ and BO₄ tetrahedra through common vertices led to tetrahedral ribbons $\infty \{[\text{BP}_2\text{O}_8]^{3-}\}$, which were arranged around 6₅ screw axes to form helices. By alternating linkage of corner-sharing PO₄ with BO₄ the helix ribbons were built up from four-ring group linkage. Each BO₄ tetrahedron was linked to four PO₄ groups *via* bridging oxygen atoms as was shown in **Figure 2**. Neighboring ribbons were interconnected by Fe^{II}/Fe^{III}O₄(H₂O)₂ octahedra leading to an infinite three-dimensional open-framework structure. Each mixed valence Fe^{II}/Fe^{III} octahedra shared two corners with two PO₄ tetrahedra in each ribbon. The arrangement of the *cis*-oriented water molecules on the Fe^{II}/Fe^{III} centers led to additional channels with size 4.89×4.89 Å². The two *cis*-positioned ligands O_{H₂O}(3) to Fe^{II}/Fe^{III} center formed hydrogen bonds with O(1), O(2) and O(5), and distance with O(3)⋯O(1) 3.25 Å, O(3)⋯O(2) 3.12 Å and O(3)⋯O(5) 3.22 Å. **Figure 3** was a section of the crystal structure as viewed along the hexagonal *c* axis.

The bulky ammonium ions were twisted around tetrahedral ribbons and located inside the free loop of the helical ribbons $\infty [\text{BP}_2\text{O}_8]^{3-}$ closer to the inner wall of helical ribbons, effecting on balancing charge and stabilizing borophosphate ribbons. Because of two disordered positions, that was only 0.77(4) Å apart from each other, were closer

the neutral water molecules inside and also closer to the inner wall of the helical channels $\infty \{[\text{BP}_2\text{O}_8]^{3-}\}$. The channel size derived from crystallographic O...O distance was $8.73 \times 8.73 \text{ \AA}^2$. This reasonable arrangement indeed explained the crystal structure of the title compound. The reactant thiocarbamide played a key role in forming process of single crystals. It decomposed to release ammonium ions, by adjusting pH value and providing the cationic ions to meet the crystal growth needs.

Figure 3 A section of the crystal structure as viewed along the hexagonal *c* axis



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