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$Fe(H_2O)_2BP_2O_8{\cdot}H_2O$, a First Zeotype Ferriborophosphate with Chiral Tetrahedral Framework Topology

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Aluminosilicate compounds have been studied because of their applications as catalysts, molecular sieves and ion exchangers.[1] In the last years Al^{3+} and Si^{4+} in the zeolite frameworks have been either completely or partially substituted with a variety of atoms. For example, alumino- (or gallo-) phosphates and zinco- (or beryllo-) phosphates or -arsenates have been found to be isotypic with known aluminosilicate molecular sieves.[2,3] Of fundamental importance is the synthesis of new zeolitic materials with novel structural properties because the utility of these crystalline materials is intimately correlated to their geometrical features.[4] A microporous zincoborate[5] is also known. Recently, there have been considerable efforts made in synthesizing novel borophosphate compounds. This has led to the preparation of new compounds with quite different anionic partial structures, such as oligomeric units, chains, ribbons, layers, and three-dimensional frameworks.[6] Sevov[7] reported $CoB_2P_3O_{13}(OH){\cdot}C_2H_{10}N_2$ as the first microporous metal borophosphate. Zubieta et al. reported the synthesis and structures of VOBOPO$^-$, a three-dimensional oxovanadium borophosphate,[8] and VOBOPO^{2-}, the first oxometalate borophosphate molecular cluster.[9] Another vanadium borophosphate with cluster anions were synthesized by using an organic template characterized by Bontchev et al.[10,11]

The first tetrahedral framework structural borophosphate compounds were synthesized by Kniep et al.,[12] zincoborophosphates, $K[ZnBP_2O_8]$ and $A[ZnBP_2O_8]$ ($A = NH_4^+, Rb^+, Cs^+$). The topologies of compounds display a close relationship to tecto-aluminosilicates (feldspar family and gismondine).

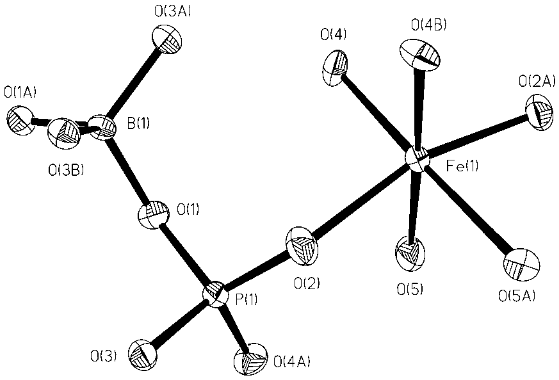

Figure 1. ORTEP view of coordination environments for Fe, B, and P atoms in the asymmetric unit. Atom labels having "A" or "B" refer to symmetry-generated atoms.

In this communication we describe the hydrothermal synthesis[13] and single-crystal X-ray structural characterization of $Fe(H_2O)_2BP_2O_8{\cdot}H_2O$, a hydrated iron borophosphate with a chiral, tetrahedral framework topology.[14,15] On the other hand hydrothermal synthesis and structure of $M^IM^{II}(H_2O)_2[BP_2O_8{\cdot}H_2O$ (M^I = Na, K and M^{II} = Mg, Mn, Fe, Co, Ni and Zn) type of compounds have been reported by Kniep et al.[16]

The asymmetric unit consists of one unique tetrahedral B^{3+} site, one unique tetrahedral P^{5+} site, and one unique Fe^{3+} site. Both B^{3+} and Fe^{3+} sites are located on the crystallographic 2-fold axis that is aligned along the unit cell *c* axis. Oxygen sites (O1, O2, O3, and O4) are on general positions and they are all bicoordinated between two framework polyhedral atom sites (i.e., P, Fe, or B) (Figure 1). The fifth oxygen site (O5) is coordinated to the iron site and because of the 2-fold symmetry on the iron site, each iron is actually bonded to two O5 atoms, making iron octahedrally coordinated.

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(13) The title compound $Fe(H_2O)_2BP_2O_8{\cdot}H_2O$ was synthesized under mild hydrothermal conditions: 5.675 g of $FeCl_2{\cdot}4H_2O$, 1.758 g of H_3BO_3, 7.550 g of $(NH_4)_2HPO_4$, and 7.712 g of 85% H_3PO_4 were mixed in 5 g of distilled water and treated under stirring with 85% H_3PO_4, until the components dissolved completely; the pHs of initial solutions were 2. The clear solutions were heated without boiling to concentrate to about 15 mL then transferred to Teflon-coated steel autoclaves (degree of filling were 65%) and heated at 180 °C for 2 days. The crystalline products were filtered off in a vacuum, washed with distilled water, and dried at 60 °C.

(14) Suitable hexagonal bipyramidal crystals were glued to a thin fiber with epoxy resin and mounted on a Bruker Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å operating at 45 kV and 40 mA). Room temperature intensity data were collected with scans (width of 0.30 Å and exposure time of 30 s per frame). The empirical absorption corrections were based on the equivalent reflections and other possible effects such as absorption by the glass fibre were simultaneously corrected. The structure was solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHEXTL running on Silicon Graphics Indy 5000.

(15) Crystal data for $Fe(H_2O)_2BP_2O_8{\cdot}H_2O$, $M = 310.65$, space group $P6(5)22$, $a = 9.4583(8)$ Å, $c = 15.707(2)$ Å, $V = 1216.9(2)$ Å^3, $Z = 6$, $D_c = 2.543$ g/cm^3, $\mu = 2.306$ mm^{-1}, $2.49° < \theta < 28.27°$, $R(F) = 3.01\%$, $wR(F2) = 7.50\%$, GOF = 1.221 for 982 observed reflections with $I > 2.0\ \sigma(I)$.

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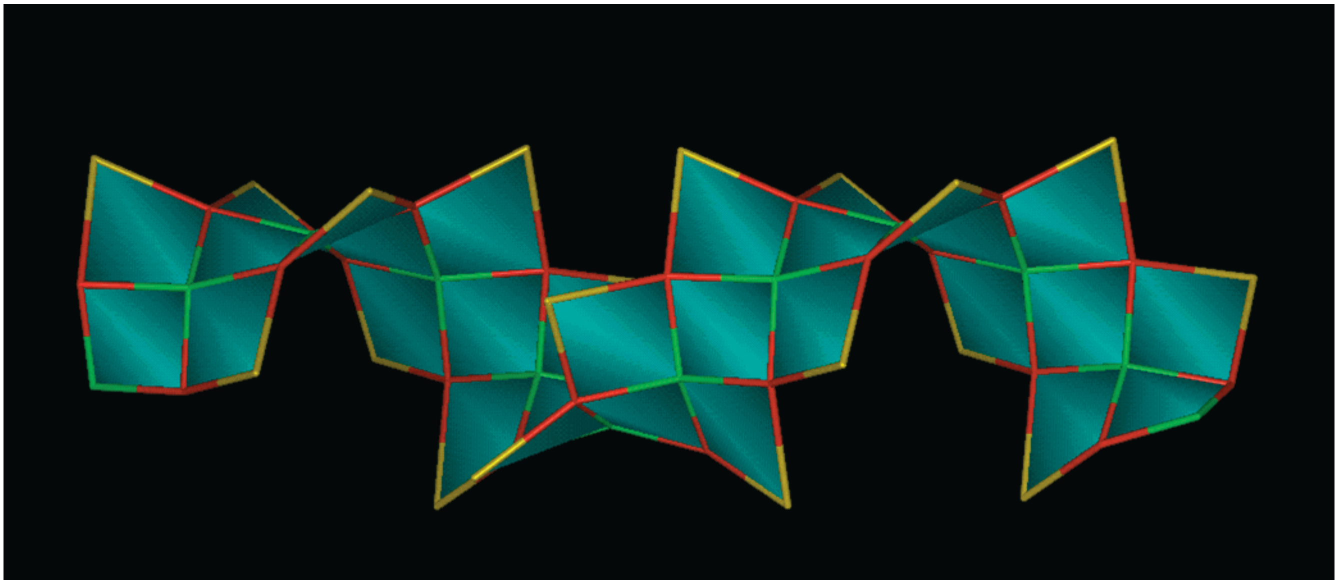

Figure 2. Helical channel along the hexagonal *c* axis. Bridging oxygen atoms are omitted for simplicity. Key: red, phosphorus; green, boron; yellow, iron.

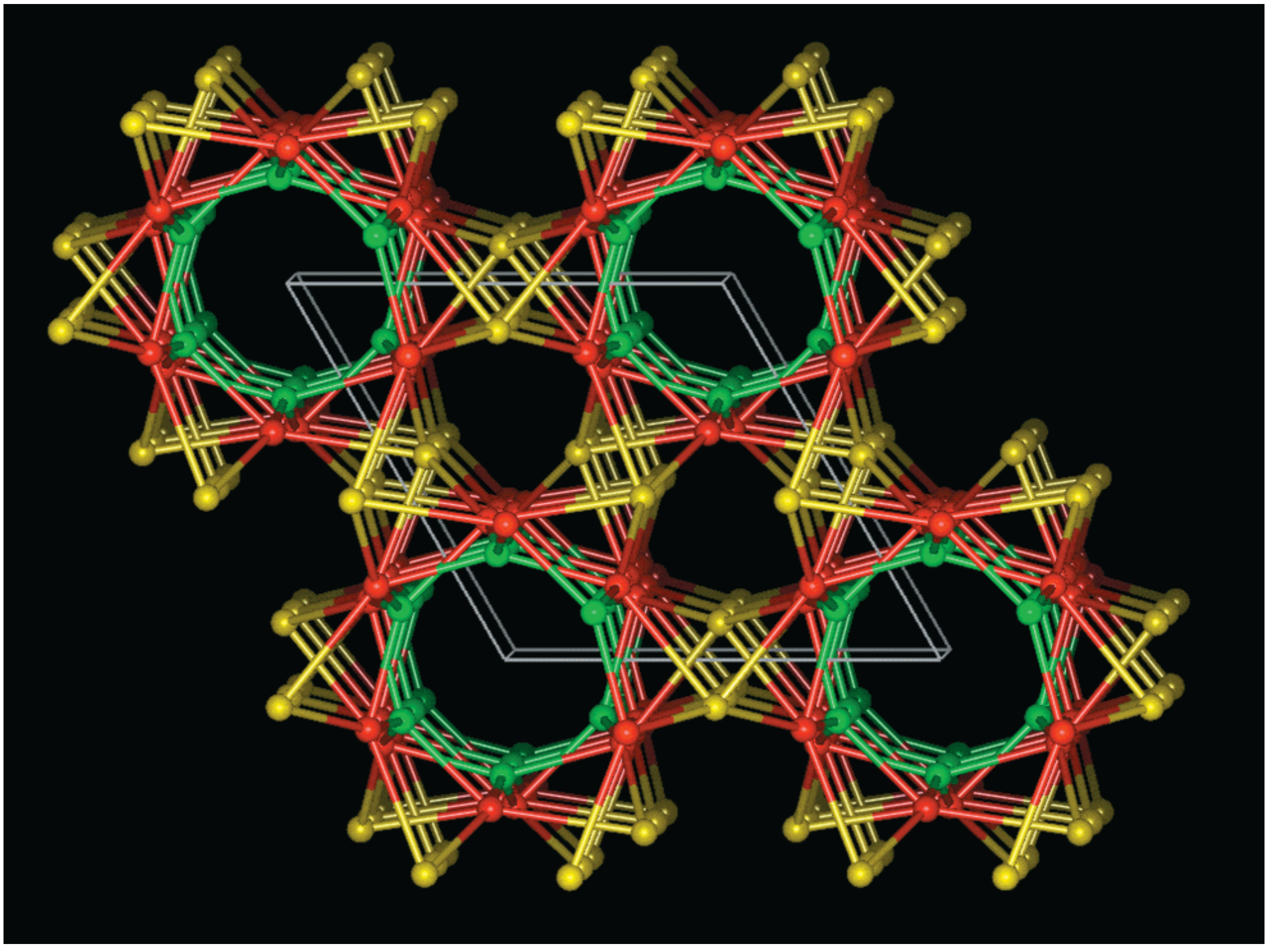

Figure 3. Projection of the three-dimensional network down the unit cell *c* axis. Bridging oxygen atoms are omitted for simplicity. Key: red, phosphorus; green, boron; yellow, iron.

The sixth oxygen site is occupied by an extraframework water molecule, and this water molecule is also located on the 2-fold axis.

Even though the iron site is octahedrally coordinated, it is in fact four-connected to the other part of the framework. Such a feature is not uncommon among zeolite-type materials. One of the well-known examples is VPI-5 in which a significant fraction of aluminum sites are octahedrally coordinated because of the coordination water molecules. In fact, the International Zeolite Association has already assigned a structure type code “CZP” to such a topology based on an earlier discovered hydrated sodium zincophosphate.[17] Compared to this zincophosphate, the title compound re-

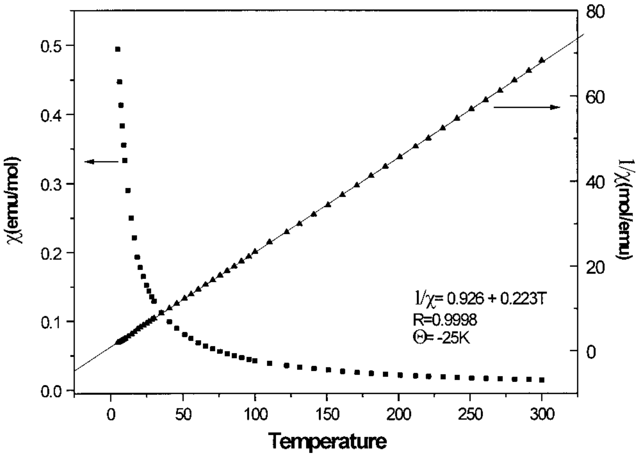

Figure 4. Magnetic susceptibility and inverse magnetic susceptibility curve vs temperature for $Fe(H_2O)_2BP_2O_8{\cdot}H_2O$.

ported here is different in several aspects. First, the framework consists of three ordered polyhedral centers. While the ternary zeolite type materials such as metal substituted aluminophosphates are very common,[18] tetrahedral atom sites are usually not completely ordered. Second, the combination of the three polyhedral atom types (i.e., Fe, B, and P) is very uncommon for zeolite-type materials. Since the discovery of aluminophosphate molecular sieves, there have been lots of efforts aimed at the synthesis of 4-connected boro- and ferriphosphates. Unfortunately, little success has been achieved as far as 4-connected frameworks are concerned. This work demonstrates that by combining boron and iron with phosphorus in a ternary system a zeolite-type framework topology can be generated.

As expected for a zeolite-type topology, only B−O−P and Fe−O−P linkages are present in the title compound. In particular, there is no B−O−Fe connection. It is of interest to note that the framework is neutral and unlike the related zincophosphate, there is no charge balancing cations blocking channels in the title compound (Figures 2 and 3). In addition, the crystal can be prepared in pure chiral forms [the refined Flack parameter is 0.01(4)], rather than the racemic crystal as reported for the above zincophosphate.

In several aspects, the title compound is related to the famous hydrated ferrialuminophosphate, cacoxenite.[19] Both are hydrated ternary phosphates and organic molecules are not necessary for the formation of their frameworks. The successful synthesis of the title compound clearly suggests that there could be a large family of related materials with similar compositions.

The stability of the title compound to heat was analyzed with thermogravimetric analysis (TG) and differential thermal analysis (DTA) which were performed on a Netzsch Simultaneous Thermal Analysis (STA) 409 system in static air with a heating rate of 5 °C/min from 30 to 1100 °C using a sample weight of 50.0 mg. Thermal dehydration of $Fe(H_2O)_2BP_2O_8{\cdot}H_2O$ is a two-stage process. In the first step (100−235 °C) 2 mol of water (1 mol of water in the channel and 1 mol of water coordinated to Fe) were released; the last mole of water was lost at 500 °C.[16] X-ray powder diffraction patterns of heated products at 100, 235, 400, and 600 °C for 2 h at each temperature showed that they are still crystalline at 235 °C and become amorphous after heating at 400 °C. The unit cell volume decreases during the heating process.

Susceptibility measurements were carried out using Quantum Design MPMS-5S Magnetic Properties Measuring System. Data were collected over the temperature range 5−300 K with an applied field of 100 G. The magnetization (Figure 4) of the title compound is paramagnetic down to 5 K of the Curie−Weiss type within the measured range of 5−300 K with $\Theta = -25$ K indicative of antiferromagnetic interactions between iron centers. The effective magnetic moment derived from this measurement, 5.93 μ_B, is in good agreement with the expected 5.9−6.0 μ_B for weak field octahedral coordination and five unpaired electrons in Fe(III).

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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