SHORT PAPER

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Synthesis and structural characterisation of a new ferrous-ferric borophosphate: $(NH_4)_{0.5}Fe^{II}_{0.5}Fe^{III}_{0.5}(H_2O)_2BP_2O_8$ $0.5H_2O$[†]

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A new ferrous-ferric borophosphate was synthesised by hydrothermal conditions and structurally characterised by X-ray single crystal diffraction, IR, TGA, XPS as well as magnetic measurement.

Keywords: open-framework, borophosphate, single crystal, synthesis

Open-framework borophosphate solids have received much attention due to potential application as functional materials. Although the ferric borophosphate compounds, $Fe(H_2O)_2BP_2O_8$ $\cdot H_2O$(**1**) and $(NH_4)_{0.4}Fe^{II}_{0.55}Fe^{III}_{0.5}(H_2O)$ $[BP_2O_8]$ $0.6H_2O$(**2**) have been reported,[1, 2] mixed valent iron borophosphate that contains a single iron site and ammonium ions in the crystal structure has not been found due to the structural diversity and the complexity of borophosphate chemistry.[3–7] We now report the synthesis and structural characterisation of an example of this new type of borophosphate compound, $(NH_4)_{0.5}Fe^{II}_{0.5}Fe^{III}_{0.5}(H_2O)_2BP_2O_8$ $\cdot 0.5H_2O$(**3**).

The title compound was synthesised by useful adjustment of starting materials and experimental procedures. The molar ratio: $FeCl_2 \cdot 4H_2O$:H_3BO_3:H_3PO_4:NH_2CSNH_2:-H_2O = 0.5:3:1:1:11 in hydrothermal conditions at 110 °C gave the product in 49% yield based on Fe. The atomic coordinates and equivalent isotropic displacement parameters, as well as the selected bond lengths and angles are listed in Table 1 and Table 2, respectively. The asymmetric unit is shown in Fig. 1. Both Fe and B atoms are located on the crystallographic 2-fold axis that is aligned along the unit cell *c* axis and are octahedrally and tetrahedrally coordinated to adjacent oxygen atoms. The tetrahedral phosphorus atom is bonded to the Fe atom and the B atom *via* oxygen-atom bridges. Oxygen atom O(3) is coordinated to the iron and because of the 2-fold symmetry of the iron atom, each iron actually bonds to two O(3) atoms, making the iron octahedrally coordinated.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times$Å^2 10^3)

Atom	*x*	*Y*	*z*	U_{eq}
Fe	4473(1)	5527(1)	833	15(1)
P	6148(1)	7832(1)	2477(1)	14(1)
B	8490(4)	6979(7)	2500	14(1)
O (1)	4870(3)	6253(3)	2085(2)	22(1)
O (2)	6818(3)	6144(4)	480(2)	22(1)
O (3)	5170(4)	8047(4)	507(2)	32(1)
O (4)	7879(3)	8102(3)	2312(2)	16(1)
O (5)	5863(3)	7646(3)	3454(1)	14(1)
O (6)	8390(30)	9193(13)	-833	293(17)
N	7440(70)	8720(30)	-833	81(17)
H(3B)	4730(90)	8280(90)	940(30)	120(30)
H(3A)	4910(80)	8350(70)	40(20)	80(20)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 2 Selected bond lengths (Å) and angles (°)

Fe–O(1)^a	2.053(3)	O(1)–Fe–O(3)	87.41(12)
Fe–O(1)	2.053(3)	O(2)–Fe–O(3)	86.18(13)
Fe–O(2)	2.065(3)	O(1)–Fe–O(3)^a	82.32(11)
Fe–O(2)^a	2.065(3)	O(2)^a–Fe–O(3)^a	86.18(13)
Fe(1)–O(3)	2.191(3)	O(1)^a–Fe–O(2)	90.48(10)
Fe–O(3)^a	2.191(3)	O(1)–Fe–O(2)^a	90.48(10)
P–O(1)	1.504(3)	O(1)^a–Fe–O(3)	82.32(11)
P–O(2)^b	1.505(3)	O(1)–P–O(2)^b	114.36(16)
P–O(4)	1.547(3)	O(1)–P–O(4)	110.67(16)
P–O(5)	1.551(2)	O(2)^b–P–O(4)	106.61(16)
B–O(4)^c	1.469(4)	O(1)–P–O(5)	106.53(14)
B(1)–O(4)	1.469(4)	O(2)^b–P–O(5)	111.38(14)
B(1)–O(5)^d	1.469(4)	O(4)–P–O(5)	107.10(14)
B–O(5)^e	1.469(4)	O(4)–B–O(5)^d	111.97(14)
O(2)–P(1)^d	1.505(3)	O(4)–B–O(5)^e	113.83(13)
O(5)–B(1)^b	1.469(4)	O(6)–N	0.77(4)

Symmetry transformations used to generate equivalent atoms: ^{a}-y+1, -x+1, -z+1/6; ^{b}y, -x+y+1, z+1/6; ^{c}-x+y+1, y, -z+1/2; ^{d}x-y+1, x, z-1/6; ^{e}y, x, -z+2/3.

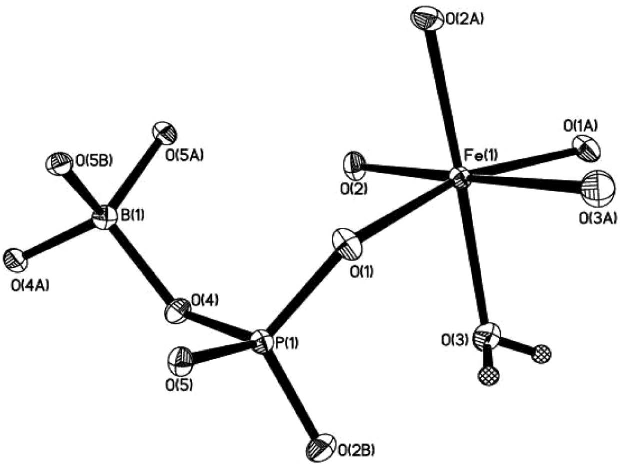

Fig. 1 ORTEP coordination environment of Fe, P and B atoms in the asymmetric unit

The condensation of PO_4 and BO_4 tetrahedra through common vertices leads to tetrahedral ribbons $^1_\infty\{[BP_2O_8]^{3-}\}$, which are arranged around 6_5 screw axes to form a helical polyanion. The helical ribbons are built up from four-ring atoms through alternating linkage of corner-sharing PO_4 with BO_4 groups. Each BO_4 tetrahedron is linked to four PO_4 groups *via* oxygen atoms. The statistically distributed equimolar Fe^{II}/Fe^{III} ions link two terminal oxygen atoms of the phosphate groups in the borders of the ribbons to form a three-dimensional open-framework structure. The compound

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

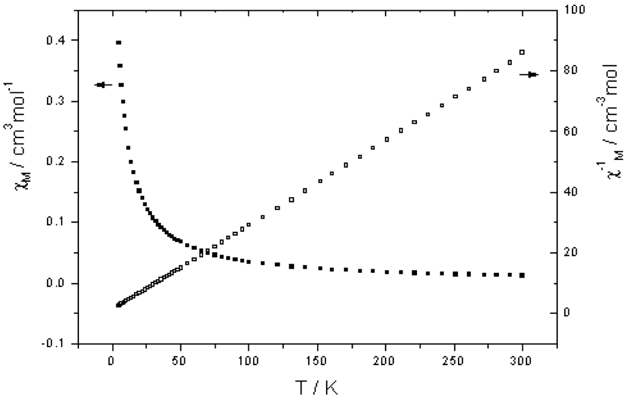

Fig. 2 Magnetic susceptibility and inverse magnetic susceptibility curve *vs* temperature.

is isostructural with the compound $(NH_4)_{0.4}Fe^{II}_{0.55}Fe^{III}_{0.5}(H_2O)[BP_2O_8]·0.6H_2O$, but the noticeable difference in bond distance caused by iron coordination in the title compound and that reported in the literature is obvious. For example, the shorter P–O distance d_{av} = 1.526 Å, compared to P–O d_{av}=1.536 Å affects the geometry of the connecting BO_4 tetrahedra, ideal and deformed in (**3**) and (**2**). Also, the Fe–O(H_2O) distance is obviously shorter d = 2.191 Å than d_{av} = 2.235 Å in (**3**) and (**2**).

The formula of the title compound is obtained from the results of thermal analysis, element analysis and bond sum calculation as well as charge balance calculation. The mixed valent system Fe^{II}/Fe^{III} was confirmed by X-ray-photoelectron spectroscopy, and the bond valence sum[8] (Σs = 2.24 for Fe^{2+} and Σs = 2.4 for Fe^{3+}). Element analysis, IR and thermal analysis revealed 2.69% nitrogen and the presence of nitrogen in the crystal structure of the compound. The ammonium ions and channel water molecules of the statistically disordered distribution are located within the helical ribbon channels. Two positions are only 0.77(4) Å apart from each other. The bulky ammonium ions are shifted to the inner wall of the helical ribbons, balancing charge and stabilising the borophosphate ribbons. The water molecules are positioned inside helical ribbons closer to the inner wall of the helical channels.

Figure 2 shows the magnetic susceptibility and inverse magnetic susceptibility of the title compound plotted as a function of temperature. The $\chi_M T$ value decreases with decreasing temperature, indicating the antiferromagnetic interactions. At higher temperature $110<T<300$ K, the $\chi_M T$ value remains constant at 3.5 cm^{3}mol^{-1}K, paramagnetic and obeys the Curie-Weiss law: $\chi_M = C/(T - \theta)$, where C = 3.575 cm^{-3} K/mol and θ = -3.426 K. From the relation $C = NB\mu_{eff}/3\ k_B$[9] we obtain the effective magnetic moments $\mu_{eff} = 5.3\mu_B$, which is in agreement with the expected value of $5.4\mu_B$ for high spin $Fe^{II}$and Fe^{III} of weak field octahedral coordination for the same ratio of Fe^{II} and Fe^{III}. Below 110 K, the magnetic properties are dominated by antiferromagnetic interactions.

Experimental

The iron state was analysed by X-ray-photoelectron spectroscopy. IR spectra were recorded on a Nicolet NEXUS-670 FT-IR spectrometer in KBr in the range 400–4000 cm^{-1}. Element analysis were obtained with an Elementar vario EL III instrument. DTA/TG studies were carried out at a heating rate of 3 °C/min in air from 25 °C to 800 °C with a TGA/SDTA851^e instrument using a sample weight of 22 mg. Magnetic data at low temperature were obtained from 5 to 300 K in a magnetic field of 100 Oe on a Quantum Design MPMS-7 Magnetometer using 50.05 mg of the compound.

Synthesis of the title compound: A mixture of $FeCl_2·4H_2O$, H_3BO_3, H_3PO_4 (85 wt%), NH_2CSNH_2 and H_2O in molar ratio of 0.5:3:1:1:11 was loaded in a sealed thick wall Pyrex tube, and then kept in an oven at 110 °C for 6 days. Black octahedral crystals were obtained after washing with deionised water. Element analysis N: 2.69%, H: 2.31%; IR (cm^{-1}): 3475, 3272, 1638, 1436, 1170, 1020, 997, 958, 843, 677, 640, 566, 518 and 487 cm^{-1}. The TG curve showed a three step mass loss with a total loss of 18% (cal.17%). The first and second stages, being not obviously distinguished, totally lost 2.5 mol water molecules, and the final stage at 600 °C released approximately 4% NH_3.

Crystal data: $(NH_4)_{0.5}Fe^{II}_{0.5}Fe^{III}_{0.5}(H_2O)_2BP_2O_8 \cdot 0.5H_2O$, M = 310.4, Hexagonal, space group P6$_5$22, a = 9.452(2) Å, c = 15.698(5) Å, V = 1214.4(5) Å^3, D_c = 2.549 g/cm^3, Z = 6, μ = 2.311 mm^{-1}, T = 298(2) K. 4292 reflections measured, 590 unique (R_{int} = 0.0289) which were used in all calculations. The final R induces ($I > 2\sigma(I)$): R_1 = 0.0206, wR_2 = 0.0569; the final R (all data): R_1 = 0.0211, wR_2 = 0.0571. The data for the crystals (0.20 mm × 0.15 mm × 0.15 mm) were collected on a Bruker SMART-CCD diffractometer using a Mo anode (λ = 0.71073 Å) and graphite monochromator. Intensity data with 2θ value in the range 4.98–46.48° were collected using ω scans. The structure was determined by direct method, and the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 using the SHELXTL program package. Hydrogen atoms of partial water molecules were directly located from a difference Fourier map and included in the structure. Full crystallographic details had been deposited at Fachinformationszentrum Karlsruhe Center (CSD-412989).

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