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Hydrothermal synthesis, crystal structure, and magnetic properties of a novel organo-templated iron(III) borophosphate: $(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$

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ABSTRACT

The organo-templated iron(III) borophosphate $(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ was prepared under mild hydrothermal conditions (at 443 K) and the crystal structure was determined from single crystal X-ray data at 295 K (monoclinic, $P2_1/c$ (No. 14), $a = 5.014(2)$ Å, $b = 9.309(2)$ Å, $c = 20.923(7)$ Å, $\beta = 110.29(2)^\circ$, $V = 915.9(5)$ Å^3, $Z = 2$, $R1 = 0.049$, $wR2 = 0.107$ for all data, 2234 observed reflections with $I > 2\sigma(I)$). The title compound contains a complex inorganic framework of borophosphate trimers $[BP_2O_8(OH)_2]^{5-}$ together with $FeO_4(OH)(H_2O)$- and $FeO_4(OH)_2$-octahedra forming channels with ten-membered ring apertures in which the diaminopropane cations are located. The magnetization measurements confirm the Fe(III)-state and show an antiferromagnetic ordering at $T_N \approx 14.0(1)$ K.

1. Introduction

Microporous materials are of great interest from both the industrial and academic point of view due to their catalytic, adsorbent, and ion-exchange properties [1–3]. The presence of large cavities in the open framework structures may provide a large internal surface area together with a large number of catalytic sites. Several investigations dealing with organically templated iron phosphates have evidenced a rich structural chemistry in these systems [4]. Following these observations we started our research on iron borophosphate including organic templates. Although many iron borophosphates without or with alkali metal/ammonium ions had been reported [5], only two organically templated iron borophosphates are known up to now: $(C_2H_{10}N_2)Fe^{II}[B_2P_3O_{12}(OH)]$ [6] and $(C_4H_{12}N_2)_3Fe^{III}{}_6(H_2O)_4[B_6P_{12}O_{50}(OH)_2]\cdot 2H_2O$ [7]. Here, we report on the hydrothermal synthesis, crystal structure, and magnetic properties of the novel organo-templated iron(III) borophosphate $(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$, representing a templated 3D framework structure.

2. Experimental section

2.1. Synthesis

$(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ was prepared under mild hydrothermal conditions at 443 K. A mixture of 0.811 g $FeCl_3\cdot 6H_2O$ (Alfa, 99.8%), 1.484 g H_3BO_3 (Alfa, 99.9%), 0.822 g $C_3H_{10}N_2$ (1,3-diaminopropane, **DAP**, Aldrich, 99%) and 1.26 g H_3PO_4 (85%, Merck, p.a.) (molar ratio of 3:24:11:11), together with 7.5 ml H_2O was stirred at 333 K for 2 h. Meanwhile 0.8 ml 37% HCl was added to adjust the pH value to 1.0. The clear colourless solution was transferred into a Teflon autoclave ($V = 10$ ml, degree of filling 60–70%) and treated at 443 K for eight days. Colourless prismatic crystals of $(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ up to 0.2 mm in length were separated from the mother liquor by vacuum filtration followed by washing several times with deionized water and drying at 333 K in air. During our study on the preparation of the title compound, we found that the H_3BO_3 content in the starting mixture has a large effect on the final product. By keeping all the other parameters constant, the use of only half amount of H_3BO_3 (0.742 g) leads to lower yield of the title phase and an additional unidentified iron phosphate. By increasing the boron content to 2.968 g H_3BO_3, the crystal size of the title compound increases and some additional small amounts of an unknown white fine powder is observed. By this, the amount of boric acid in the starting mixture appears to be the most

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Table 1
Crystallographic data and refinement results of $(C_3H_{12}N_2)Fe^{III}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ (e.s.d).

Molecular formula	$(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$
Space group	Monoclinic, $P2_1/c$ (No. 14)
a (Å)	5.014(2)
b (Å)	9.309(2)
c (Å)	20.923(7)
β (deg)	110.29(2)
V (Å^3)/Z	915.9(5)/1
ρ_{calc} (g cm^{-3})	2.579
μ (Mo$K\alpha$) (mm^{-1})	2.813
Crystal size (mm^3)	$0.12 \times 0.06 \times 0.04$
Diffractometer	Rigaku R-axis RAPID, Mo$K\alpha$-radiation, Graphite monochromator
Scan type	ω-scan
2θ-range (deg)	6.0–60.0
$h\,k\,l$ range	$-5 \leqslant h \leqslant 6$, $-13 \leqslant k \leqslant 13$, $-29 \leqslant l \leqslant 22$
R_{int}/R_σ	0.032/0.046
Measured/unique/observed ($I > 2\sigma(I)$) reflections	5837/2284/2234
Number of parameters	178
$R1/wR2$ ($I > 2\sigma(I)$)	0.048/0.107
$R1/wR2$ (all data)	0.049/0.107
Goodness-of-fit (for F^2)	1.256
Residual electron density (min/max) (e Å^{-3})	−1.233/1.735

Table 2
Atomic coordinates and equivalent/isotropic displacement parameters (Å^2) in the crystal structure of $(C_3H_{12}N_2)Fe^{III}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ (e.s.d).

Atom	x	y	z	U_{eq}/U_{iso}
Fe1	0.40093(12)	0.68831(5)	0.78393(3)	0.00808(12)
Fe2	0.0000	0.0000	0.0000	0.00754(16)
P1	0.2184(2)	0.35277(9)	0.78970(5)	0.00746(19)
P2	0.3803(2)	0.89334(9)	0.91624(5)	0.00758(19)
B1	0.4622(9)	0.6345(4)	0.6378(2)	0.0071(7)
O1	0.4604(6)	0.5851(3)	0.70421(14)	0.0122(6)
$H1_{O1}$	0.429(14)	0.499(7)	0.707(3)	0.039(18)
O2	0.4403(6)	0.2857(3)	0.85513(14)	0.0102(5)
O3	0.1322(6)	0.8651(3)	0.94073(15)	0.0107(5)
O4	0.3400(6)	0.0474(3)	0.88445(14)	0.0111(5)
O5	0.2087(6)	0.5144(3)	0.80276(15)	0.0120(6)
O6	0.8243(7)	0.1293(3)	0.91461(15)	0.0125(6)
$H2_{O6}$	0.932(13)	0.140(6)	0.901(3)	0.025(16)
O7	0.6600(6)	0.8855(3)	0.97539(15)	0.0110(5)
O8	0.6753(6)	0.8302(3)	0.77017(14)	0.0115(5)
O9	0.3746(7)	0.7828(3)	0.86235(15)	0.0163(6)
O10	0.0687(6)	0.7846(3)	0.72135(15)	0.0145(6)
O11	0.7967(7)	0.6042(4)	0.85416(18)	0.0203(7)
$H3_{O11}$	0.895(15)	0.561(8)	0.838(4)	0.05(2)
$H4_{O11}$	0.899(19)	0.670(9)	0.875(5)	0.08(3)

Table 3
Crystal structure of $(C_3H_{12}N_2)Fe^{III}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$: selected bond lengths (Å) and angles (deg) (e.s.d).

Fe1–O9	1.906(3)	O9–Fe1–O10	93.91(13)	O5–Fe1–O1	89.84(11)
–O10	1.944(3)	O9–Fe1–O5	91.25(12)	O8–Fe1–O1	83.68(11)
–O5	1.992(3)	O10–Fe1–O5	98.48(13)	O9–Fe1–O11	84.45(14)
–O8	1.998(3)	O9–Fe1–O8	94.35(12)	O10–Fe1–O11	173.40(13)
–O1	2.034(3)	O10–Fe1–O8	94.02(13)	O5–Fe1–O11	87.95(13)
$-O11_{H2O}$	2.165(3)	O5–Fe1–O8	165.92(12)	O8–Fe1–O11	79.75(13)
		O9–Fe1–O1	175.72(14)	O1–Fe1–O11	91.44(13)
		O10–Fe1–O1	90.03(12)		
Fe2–O7	1.923(3)	O7–Fe2–O7	180.0(2)	O3–Fe2–O6	87.93(12)
–O7	1.923(3)	O7–Fe2–O3	93.42(11)	O3–Fe2–O6	92.07(12)
–O3	2.031(3)	O7–Fe2–O3	86.58(11)	O7–Fe2–O6	91.08(12)
–O3	2.031(3)	O7–Fe2–O3	86.58(11)	O7–Fe2–O6	88.92(12)
$-O6_H$	2.080(3)	O7–Fe2–O3	93.42(11)	O3–Fe2–O6	92.07(12)
$-O6_H$	2.080(3)	O3–Fe2–O3	180.00(14)	O3–Fe2–O6	87.93(12)
		O7–Fe2–O6	88.92(12)	O6–Fe2–O6	180.00(17)
		O7–Fe2–O6	91.08(12)		
P1–O10	1.516(3)	O10–P1–O5	110.55(16)	O10–P1–O2	108.42(17)
–O5	1.533(3)	O10–P1–O8	113.45(17)	O5–P1–O2	107.01(16)
–O8	1.536(3)	O5–P1–O8	108.74(15)	O8–P1–O2	108.46(16)
–O2	1.564(3)				
P2–O7	1.517(3)	O7–P2–O9	110.29(17)	O7–P2–O4	109.76(16)
–O9	1.520(3)	O7–P2–O3	110.43(16)	O9–P2–O4	109.83(17)
–O3	1.524(3)	O9–P2–O3	108.98(17)	O3–P2–O4	107.50(15)
–O4	1.564(3)				
$B1–O1_H$	1.467(5)	O1–B1–O6	111.7(3)	O1–B1–O2	108.3(3)
$-O6_H$	1.475(6)	O1–B1–O4	110.6(3)	O6–B1–O2	108.0(3)
–O4	1.476(5)	O6–B1–O4	109.6(3)	O4–B1–O2	108.6(3)
–O2	1.480(4)				
O1–H1	0.82(7)	O11–H3	0.79(8)		
O6–H2	0.70(6)	O11–H4	0.82(9)		
N1–C3	1.519(9)	N1–C3–C1	124.1(10)		
N2–C2	1.47(2)	C3–C1–C2	100.0(12)		
C1–C2	1.518(10)	C1–C2–N2	77.1(16)		
C1–C3	1.30(2)				

important factor to obtain a pure reaction product. The phase purity of samples applied for further properties investigations was checked by elemental analyses and powder X-ray diffraction.

2.2. Crystal structure determination

A colourless prismatic single crystal of $(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ ($0.12 \times 0.06 \times 0.04$ mm^3) was fixed on a glass fibre with two-component glue. X-ray data were collected at 295 K using a RIGAKU R-Axis RAPID diffractometer, equipped with curved R-axis Rapid imaging plate detector and a three-circle goniometer (Mo$K\alpha$ radiation, graphite monochromator). Intensity data were collected in the angular range $2.42^\circ \leqslant 2\theta \leqslant 73.82^\circ$. The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied. The structure was solved by direct methods in the space group $P2_1/c$ (No. 14) using the program SHELXS-97-2 [8]. Fourier calculations and subsequent full-matrix least-squares refinements were carried out by using SHELXL-97-2 [9], applying neutral atom scattering factors. The framework atom positions were all located and refined. After including anisotropic displacement parameters in the refinement, the hydrogen atoms bonded to oxygen could be located from difference Fourier maps and were refined without any restraints. The template atom positions (C and N) could not be directly located from difference Fourier maps, the procedure of how to identify them is described below. Details of the data collection and relevant crystallographic data are summarized in Table 1.[1] Atomic positions and displacement parameters for $(C_3H_{12}N_2)Fe^{III}{}_6(H_2O)_4[B_4P_8O_{32}(OH)_8]$ are given in Table 2, selected bond lengths and angles in Table 3, respectively.

The electron density of the $(C_3H_{12}N_2)^{2+}$ ions in Fourier maps (see Supporting information) clearly shows that it represents a continuous distribution which indicates a disorder of the $(C_3H_{12}N_2)^{2+}$ ions. Based on the results of the chemical analyses (see below) showing that only one $(C_3H_{12}N_2)^{2+}$ ion contributes to the formula unit, we tried to locate the C and N atoms by constraining their occupancies. The final results are shown in Fig. 1. Both C and N atom positions are only partially occupied. The organic molecules are present in two different orientations related by a centre of symmetry. Due to the overlap of the DAP molecules in a way that N1 is shared by two different orientations of the

[1] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-715705. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).