Synthesis and Structure of the First Protonated Zincoborophosphate (H₃O)[Zn(H₂O)₂]BP₂O₈·H₂O

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The solid acid of the first protonated zincoborophosphate $(H_3O)[Zn(H_2O)_2]BP_2O_8 \cdot H_2O$ **1** was soventothermally synthesized by the reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and H_3BO_3 with H_3PO_4 in a mixed solvent and structurally characterized by single-crystal X-ray diffraction analysis. It crystallizes in the hexagonal $P6_122$ $a = 0.9604(4)$ nm $c = 1.5297(6)$ nm $V = 1.2218(8)$ nm^3 $D_c = 2.921$ g/cm^3 $Z = 6$ $F(000) = 1080$ $\mu = 3.495$ mm^{-1}. The structure features that the tetrahedra-tetrahedra helices interconnected by octahedra and strong hydrogen bond interactions form a three-dimensional framework. The protonated water molecules are located at unique positions. Other characterizations by IR and thermal analysis are also described.

Keywords   soventothermal synthesis zincoborophosphate protonation helical ribbon structure

Introduction

In the last few years the search for new materials with microporous and zeolite-analogous systems has primarily focused on aluminum phosphates and aluminosilicate compounds substituted with a variety of atoms.[1-3] Cobalt-substituted aluminophosphates are systematically studied mainly due to their potential use as solid-acid catalysts. In such materials the Brønsted acid site is generated by each substitution of Al(III) by Co(II) in which a proton is needed to balance the charge.[4-7] To find new type of zeolitic materials the borophosphate materials containing both BO_4 group and PO_4 group have received much attention and may offer the vast prospect of application as new type of catalysts and the possibility for optical device. Since Sevov[8] reported the first microporous metal borophosphate $CoB_2P_3O_{13}(OH) \cdot C_2H_{10}N_2$ several kinds of borophosphate compounds with quite different anionic partial structures had been synthesized under hydrothermal conditions.[9-13] However less study is taken to understand the influence of any corresponding solvents and bond inter-

actions on the formation of new borophosphates. Our studies on synthesizing borophosphate materials with special properties have led to the preparation of the protonated zincoborophosphate $(H_3O)[Zn(H_2O)_2]BP_2O_8 \cdot H_2O$ **1** . Owing to weak interactions through the hydrogen bonds the solid acid of the protonated borophosphate has been proven to be inaccessible under a direct hydrothermal condition. Therefore the first example reported herein possibly represents a new type of borophosphate materials with potential application as solid acidic catalyst. The synthesis and structural characterization of **1** are described in the following sections.

Experimental

Single crystals were synthesized by reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and H_3BO_3 with H_3PO_4 ($w = 85\%$) in molar ratio of $1:3:2$ in a mixed solvent of ethylene glycol (0.15 mL) and hydrochloric acid solution (18% 0.1 mL). The starting materials were loaded in a thick wall Pyrex tube which was sealed *in vacuo* and held at 110 ℃ for a week. The single-phase colorless octahedral crystals were obtained after washing with deionized water in 23% yield based on Zn.

The data for the crystals (0.45 mm × 0.40 mm × 0.20 mm) were collected at 293(2) K on a Bruker SMART-CCD diffractometer using a Mo Kα radiation ($\lambda = 0.071073$ nm). and graphite monochromator Intensity data with 2θ value in the range of 4.9—51.9 were collected using ω scans. A total of 5325 reflections were collected of which 805 were unique ($R_{int} = 0.0546$). 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 SHELXITL program package. The data collection structure solution and refinement are given in Table 1.

Table 1　Crystal data and structure refinement

Formula	H_3O Zn H_2O $_2BP_2O_8$ H_2O
Crystal system	Hexagonal
Space group	$P6_122$
Unit cell dimensions	$a = 0.9604$ 4 nm
	$c = 1.5297$ 6 nm
V nm^3	1.2218 8
Z	6
D_c g/cm^3	2.912
μ mm^{-1}	3.495
F 000	1080
Crystal size mm^3	$0.45 \times 0.40 \times 0.20$
Limiting indices	$-11 \leqslant h \leqslant 11$　$-11 \leqslant k \leqslant 11$　$-18 \leqslant l \leqslant 9$
Max. and min. transmission	0.5416　0.3023
Reflections collected/unique	5325/805　$R_{int} = 0.0546$
Goodness-of-fit on F^2	1.100
Final R indices $I > 2\sigma I$	$R_1 = 0.0670$　$wR_2 = 0.1480$
R indices all data	$R_1 = 0.0672$　$wR_2 = 0.1481$
Largest diff. peak and hole/ e nm^{-3}	746 and -645

Thermal analysis was carried out at a heating rate of 3 ℃/min in nitrogen atmosphere from 25 to 800 ℃ with a TGA/SDTA851^e. IR spectrum was recorded on a Nicolet NEXUS-670 FT-IR spectrometer in the KBr matrix in the range of 400—4000 cm^{-1}.

Results and discussion

The refined atomic coordinates and equivalent isotropic parameters are listed in Table 2　and the selected bond

distances and angles are given in Table 3. The crystal structure of **1** is similar to $A_x^I M_y^{II}$ H_2O $_2BP_2O_8$ $z H_2O$　$A^I =$ Li Na K Rb Cs NH_4^+　$M^{II} =$ Mg Mn Fe Co Ni Cu Zn　$x = 0.35$—1　$y = 1$—1.3　$z = 0.2$—1 .[14-19] The asymmetric unit consists of one B atom　one P atom one Zn atom and four oxygen atoms　Fig. 1 . Both Zn and B atoms are located on the crystallographic 2-fold axis with special positions　and P and O atoms are located on crystallographic general positions. The P and B atom sites take on tetrahedral coordination　and the Zn site adopts an octahedral coordination.

The condensation of PO_4 and BO_4 tetrahedra through common vertices leads to tetrahedral ribbon　which is arranged around the 6_1 axes to form a helix and a channel filled with water molecules O_w 7　as shown in Fig. 2. Each BO_4 tetrahedron belongs to the adjacent four-rings of the tetrahedron along the helical ribbon　in such a way that all vertices of the BO_4 groups participate in bridging

Table 2　Atomic coordinates $\times 10^4$　and equivalent isotropic displacement parameters nm$^2 \times 10^{-5}$

Atom	x	y	z	$U_{eq}{}^a$
Zn	754 2	5377 1	5833	30 1
P	1626 3	7784 3	7436 2	19 1
B	-1549 11	6900 20	7500	26 4
O 1	1323 11	6224 10	7052 5	32 2
O 2	-756 10	6169 9	5424 5	24 2
O 3	175 9	8049 9	7280 4	20 2
O 4	1762 9	7584 8	8437 4	17 2
O 5	8192 17	5350 18	3666 9	82 5
O 6	9376 7	6322 7	2470 4	10 1
O 7	809 15	1620 30	7500	186 17

^{a} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3　Selected bond lengths nm and angles ° ^{a}

Zn 1 —O 1 $^{\#1}$	0.1998 7		O 1 -Zn 1 -O 2	103.6 3
Zn 1 —O 1	0.1998 7		O 1 $^{\#1}$-Zn 1 -O 2 $^{\#1}$	103.6 3
Zn 1 —O 2	0.2044 8		O 1 -Zn 1 -O 2 $^{\#1}$	93.2 3
Zn 1 —O 2 $^{\#1}$	0.2044 8		O 2 -Zn 1 -O 2 $^{\#1}$	104.1 5
Zn 1 —O 5 $^{\#3}$	0.2563 9		O 2 $^{\#2}$-P 1 -O 1	115.1 5
Zn 1 —O 5 $^{\#6}$	0.2562 9		O 2 $^{\#2}$-P 1 -O 3	106.4 4
P 1 —O 2 $^{\#2}$	0.1494 8		O 1 -P 1 -O 3	111.3 5
P 1 —O 1	0.1496 8		O 2 $^{\#2}$-P 1 -O 4	111.6 4
P 1 —O 3	0.1555 8		O 1 -P 1 -O 4	104.4 4
P 1 —O 4	0.1557 6		O 3 -P 1 -O 4	107.9 4
B 1 —O 4 $^{\#3}$	0.1466 12		O 4 $^{\#3}$-B 1 -O 4 $^{\#4}$	104.5 12
B 1 —O 4 $^{\#4}$	0.1466 12		O 4 $^{\#3}$-B 1 -O 3 $^{\#5}$	113.8 4
B 1 —O 3 $^{\#5}$	0.1498 14		O 4 $^{\#4}$-B 1 -O 3 $^{\#5}$	112.2 4
B 1 —O 3	0.1498 14		O 4 $^{\#3}$-B 1 -O 3	112.2 4
O 1 $^{\#1}$-Zn 1 -O 1	152.6 6		O 4 $^{\#4}$-B 1 -O 3	113.8 4
O 1 $^{\#1}$-Zn 1 -O 2	93.2 3		O 3 $^{\#5}$-B 1 -O 3	100.8 12

^{a} Symmetry transformations used to generate equivalent atoms　#1 x　$x - y + 1$　$-z + 7/6$　#2 $x - y + 1$　$x + 1$　$z + 1/6$　#3 $y - 1$　$-x + y$　$z - 1/6$　#4 $-x$　$-x + y$　$-z + 5/3$　#5 $-x + y - 1$　y　$-z + 3/2$　#6 $-x + 2$　$-x + y + 1$　$-z + 2/3$.
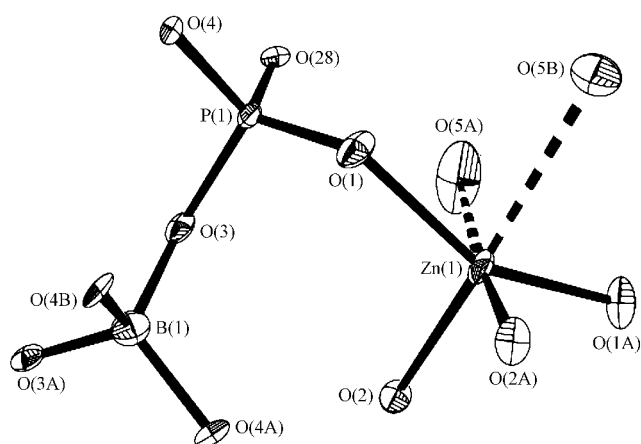
Fig. 1 ORTEP view of coordination environment for Zn B and P atoms in the asymmetric unit.
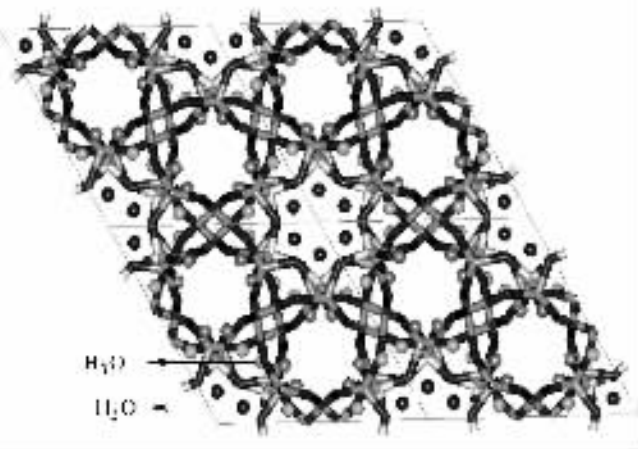

Fig. 2 A section of the crystal structure as viewed along the hexagonal *c*-axis.

functions with PO_4 tetrahedra. The phosphate groups occupy the borders of the ribbons with two terminal oxygen atoms which act as ligands along with O_w 5 from two water molecules to complete the octahedral coordination in Zn site. The Zn—O 5 distance of 0.2563 nm is longer than the intermediate length Zn—O 2 of 0.2044 8 nm indicating a weak Zn—O 5 interaction. The helical ribbons are interconnected by octahedra ZnO_4O_2 H_2O to form a three-dimensional framework.

Charge neutrality requires a proton per formula. The protons indwell the crystal structure in the form of the protonated water and can form strong hydrogen bonds with bond lengths of 0.220 and 0.228 nm for O 6 ···O 2 and O 6 ···O 1 . So extremely short hydrogen bond is uncommon. Nevertheless Haushalter[14] had discovered hydrogen bonds in the range found here in molybdenum phosphate material. The negative charge of the helical ribbons is balanced due to the presence of H_3O^+. One of the noticeable characteristics is that the H_3O^+ ions can form strong hydrogen bonds through the interactions with framework oxygen atoms to stable structure rather than by ionic bonds just as KFe H_2O $_2BP_2O_8$ H_2O.[15] Apparently the

role of the H_3O^+ ions is quite important in the formation and the stabilization of the structure. Another difference is that the H_3O^+ location in **1** is different from any of the known compounds in which the A^I ions are either located within the free thread of the helical ribbons or shifted to the inner wall of the helical channels [16-20] whereas the H_3O^+ ions in this compound are positioned inside the micropores enclosed by helical ribbons and octahedra Fig. 2 . Further more the H_3O^+ ions may act as structure-direction ions to control the solventothermal assembly of polymeric anion network.

Thermal dehydration is three stage processes Fig. 3 . The first weight loss of 9.4% is observed between 95 and 193 ℃ and attributed to the two water molecules for one crystallized water and one coordinating water. The weight loss of 4.7% at the second stage is another coordinated water between 193 and 335 ℃. A gradual loss of mass 7% at the third stage in the range of 335—684 ℃ is attributed to the loss of the protonated water molecules and the loss of hydroxyl groups which are formed by that the leaving protons combine with framework oxygen atoms. IR spectra clearly show a strong characteristic band O—H at 3400 and 1634 cm^{-1}. The results of thermal analysis and IR spectra are agreement with single crystal X-ray diffraction results.
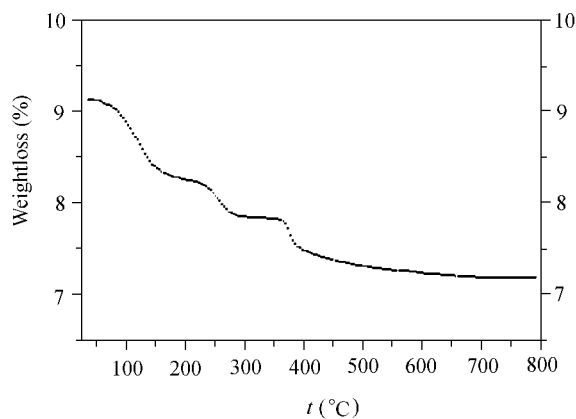

Fig. 3 Thermal analysis study of the title compound.

As might be expected the starting materials and the media role are quite important in the synthesis of H_3O - Zn H_2O $_2BP_2O_8$ H_2O. In fact if the zinc chloride is in place of Zn NO_3 $_2$ $6H_2O$ or if we used either ethylene glycol or dilute hydrochloric acid solution as solvent this compound was no obtained. The possible reasons are that less hygroscopic of nitrate suitable viscosity and the acidity are favorable to crystal growth.[21]

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