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COMMUNICATION

A Novel Open-Framework Copper Borophosphate Containing 1-D Borophosphate Anion with 10-MR Windows and 12-MR Channels†

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A novel open-framework copper borophosphate, $Na_5KCu_3[B_9P_6O_{33}(OH)_3]\cdot H_2O$ (1), has been synthesized by means of boric acid flux method. Its structure can be viewed as a 3-D open framework constructed by the connection of 10 $Cu^{II}O_6$ octahedra and 1-D (4, 4)-connected borophosphate anionic structure composed of trigonal-planar $BO_2(OH)$ groups, tetrahedral BO_4 and PO_4 groups. The compound not only features novel borophosphate anionic partial structure containing 1-D 12-MR channels, but also exhibits 15 ferromagnetic interactions and high catalytic activity for oxidative degradation of chitosan.

It is considerable interest in developing new metal borophosphates with fascinating structural architectures because of their widespread applications in optical, magnetic, catalysis 20 and ion-exchange.[1] Metal borophosphates are usually constructed by the connection of various metal polyhedra and the anionic partial structure composed of $B\Phi_3$, $B\Phi_4$ and $P\Phi_4$ groups (Φ = O or OH). Up to the present, more than 25 types of metal ions (including main-group and transition metal elements) have been 25 incorporated into borophosphates.[2] The family of metal borophosphates encompasses a rich structural variety mainly depended on all kinds of borophosphate anionic partial structures. In general, the B atom can adopt two types of coordination modes, either triangular or tetrahedral. Flexible coordination 30 behaviors of B atom give greater opportunities for the formation of the B-O-B linkages. The existence of B-O-B linkage makes it possible to build various borate motifs. Therefore, combinations of boron and phosphor groups tend to form the large group of condensation patterns of complex anions. Due to 35 the diverse arrangements of trigonal-planar $B\Phi_3$ units, tetrahedral $B\Phi_4$ and $P\Phi_4$ units (Φ = O or OH), the structures of borophosphate anions extend from isolated species, oligomers,

rings, chains, layers to three-dimensional open-frameworks with 50 various B: P ratios (B: P > 1, B: P = 1 and B: P < 1).[3]

Our interest in metal copper borophosphates is based on the following considerations: (i) The combination of the flexible coordination behavior of copper (CuO_5 square pyramid and CuO_6 octahedron) with that of boron (BO_3 triangle and BO_4 55 tetrahedron) provides greater opportunities for rational design of the large group of borophosphates with new condensation patterns of complex anions; (ii) Copper may exhibit variable oxidation states +I and +II, which is expected to enhance the structural diversity. Moreover, especially Cu^{II}-containing 60 compounds have caused great interest owing to their inherent magnetism; (iii) The asymmetric coordination of BO_3 and BO_4 units may lead to noncentro-symmetric structure with interesting optical properties. Metal borophosphates containing both BO_3 and BO_4 units are also promising nonlinear optical materials;[4] 65 (iv) Borophosphates possess excellent catalytic activity in some chemical reactions and have been used as catalysts in the chemical industry. Copper is also recognized to be an active element of the catalyst in both heterogeneous and homogeneous reaction systems. Therefore, novel copper borophosphates may 70 exhibit better catalytic activity.[5]

As part of our ongoing work,[6] herein, we have successfully isolated a novel three-dimensional open framework copper borophosphate $Na_5KCu^{II}_3[B_9P_6O_{33}(OH)_3]\cdot H_2O$ (1) with one-dimensional anionic partial structure by means of boric acid flux 75 method.[7] Its structure is constructed by the connection of $Cu^{II}O_6$ octahedra and 1-D (4, 4)-connected borophosphate anionic structure composed of trigonal-planar $BO_2(OH)$ groups, tetrahedral BO_4 and PO_4 groups. Furthermore, the catalytic activity of 1 for the oxidative degradation of chitosan with H_2O_2 80 aqueous solution in heterogeneous phase has also been investigation. To the best of our knowledge, it is the first investigation of the catalytic activity for the oxidative degradation of chitosan in the series of borophosphates.

The single-crystal X-ray diffraction analysis indicates that 1 85 crystallizes in the hexagonal with the space group of $P6_3/m$. The structure of 1 can be viewed as a three-dimensional open-framework constructed by the linkages of $Cu^{II}O_6$ octahedra and 1-D borophosphate anionic structure and achieved the charge neutrality by K^+ and Na^+ cations.

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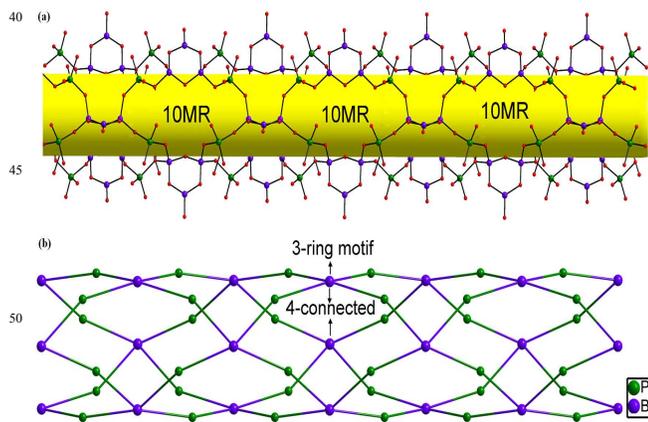[b] *Department of Chemistry, Henan Institute of Education, Zhengzhou 450046, China;*
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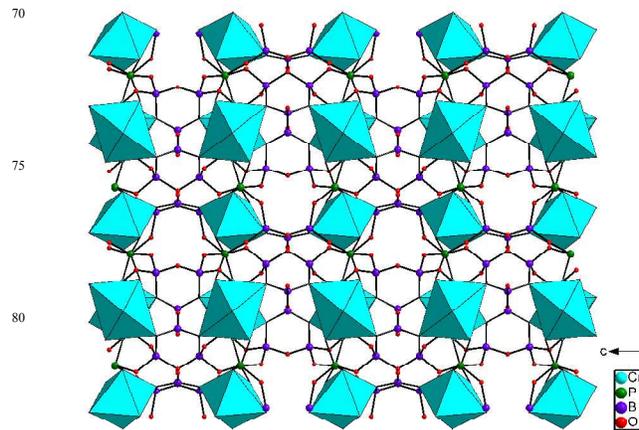
The asymmetric unit of **1** contains one crystallographically distinct Cu site, one distinct P site, two distinct B sites, one distinct K site and three distinct Na sites as shown in Fig. S1a. The B(1) atom is 3-coordinated by three oxygen atoms forming a trigonal-planar $BO_2(OH)$ group. The lengths of B(1)-O for the trigonal-planar boron group range from 1.356(6) to 1.399(12) Å. B(2) and P(1) atoms adopt tetrahedral coordination with B–O distances varying in the range of 1.430(7)–1.508(8) Å and P–O distances ranging from 1.514(4) to 1.562(4) Å. These bond lengths are in accordance with the known borophosphates.[8] Cu(1) atom is octahedrally coordinated by six oxygen atoms with the Cu–O bond lengths ranging from 1.974(4) to 2.376(4) Å. The Cu–O bond lengths in **1** are comparable to those in the previously reported copper borophosphates.[6c] Bond Valence Calculations[9] suggest that Cu, B and P atoms are present as their normal valences of +2, +3 and +5, respectively. The bond valence sums for all O atoms reveal that the O(4) site should be attributed to –OH group, which is further confirmed by IR spectrum and the thermal stability. The results are also supported by Kniep's principles: nonbridging corners of borate species in hydrated phases correspond to –OH groups.[10]

The structure of borophosphate anion $[B_6P_9O_{33}(OH)_3]^{12-}$ is made up from trigonal-planar $BO_2(OH)$ groups, BO_4 tetrahedra and PO_4 tetrahedra. Two $B(2)O_4$ tetrahedra and one trigonal-planar $B(1)O_2(OH)$ group are connected by μ_2-O atoms, resulting in a $\{B_3O_7(OH)\}$ 3-ring motif. The $\{B_3O_7(OH)\}$ motifs are further linked by the adjacent PO_4 tetrahedra *via* μ_2-O atoms, leading to the molecular structural unit of borophosphate anion $[B_6P_9O_{33}(OH)_3]^{12-}$ which possesses 12-MR *via* –B(2)–P(1)–B(2)–P(1)– linkages (Fig. S1b). According to the categories by Kniep *et al.*,[10,11] the fundamental building unit (FBU) of borophosphate anion $[B_6P_9O_{33}(OH)_3]^{12-}$ is built up from one $\{B_3O_7(OH)\}$ 3-ring motif and two PO_4 groups. The FBU of the anionic partial structure is shown in Fig. S1c. The resulting molecular structural unit is further extended to the 1-D borophosphate anionic partial structure where $\{B_3O_7(OH)\}$ motifs strictly alternate with PO_4 groups. Moreover, it is worth noting that the anionic partial structure possesses 1-D 12-MR channels running along the *c* axis

Figure 1. (a) View of the one-dimensional borophosphate anionic chain containing 12-ring channel and 10-MR windows along the *a* axis. Yellow column represents the 1-D 12-MR channel. Colour code: B, purple; P, green; O, red. (b) The (4, 4)-connected topology of one-dimensional borophosphate anionic chain. Colour code: 3-ring motif $\{B_3O_7(OH)\}$, purple; PO_4, green.

giving a diameter of *ca*. 7.6 Å × 8.8 Å and 10-MR windows along the *a* axis as given in Fig. 1a. In order to better understand the structure of 1-D borophosphate anionic partial structure, the topological approach can be applied to simplify such a 1-D architecture.[12] By considering the $\{B_3O_7(OH)\}$ 3-ring motifs as 4-connected nodes, the one-dimensional 12-MR channel can be simplified as a (4, 4)-connected topology with the Schläfli symbol of 4^4 (Fig. 1b).

Figure 2. View of the three-dimensional open-framework of **1**(K^+ and Na^+ are omitted for clarity). Colour code: CuO_6, turquoise.

The 1-D borophosphate anionic chains are interconnected *via* $Cu^{II}O_6$ octahedra acting as linkers to give rise to a 3-D open-framework structure (Fig. 2). That is, the resulting framework contains 1-D borophosphate anions of corner-linked $\{B_3O_7(OH)\}$ 3-ring motifs and PO_4 groups which are further connected by $Cu^{II}O_6$ octahedra through common vertex oxygen atoms. In the framework, each Cu^{II} is linked to two borophosphate anionic chains, and each borophosphate anionic chain is surrounded by six Cu^{II} cations. To clearly analyze the whole 3-D structure of **1**, the open-framework framework can be simplified as 8-connected topology considering borophosphate anionic chains as linear linkers as given in Fig. S2. The cations K^+ and Na^+ compensate the negative charge of the 3-D open-framework. The K^+ cations that located in the void space of 12-MR channel and all Na^+ cations adopt octahedral coordination by six oxygen atoms belonging to borophosphate anion.

The chemical composition of **1** was confirmed by the results of EDS. It indicated the presence of the elements B, P, Cu, Na, K and O (Fig. S3). The powder XRD pattern is in agreement with the simulated XRD pattern based on single-crystal structural data, proving the phase purity of the as-synthesized product as given in Fig. S4. The IR spectrum of **1** (KBr pellet) is shown in Fig. S5. The bands at 1421 and 1369 cm^{-1} correspond to the stretching and bending vibrations of BO_3 groups, while the bands in the region 1107-567 cm^{-1} (1107, 991, 915, 857, 753, 677, 601, 567 cm^{-1}) can be assigned to the asymmetric stretching and bending vibrations of BO_4, PO_4 and B-O-P groups.[13] In addition, the bands at 3398 and 1665 cm^{-1} can be attributed to the stretching and bending vibrations of –OH groups and H_2O molecules.

The thermal stability of **1** was investigated between room temperature and 800 °C with a heating rate of 10 °C/min in a dynamic N_2 atmosphere (gas flow 0.1 L/min). The studies reveal

a total mass loss of 3.44 % between 146 and 727 °C in one step ($\Delta m_{calcd}/m = 3.67\%$) (Fig. S6). In the DTG curve, one significant endothermic peak was observed at 571 °C. In this step, between 146 and 727 °C, the weight is reduced by 3.44 %, which matches the loss of 1 molecule of water ($\Delta m_{calcd}/m = 1.47$ %) and 3 molecules of –OH groups (1.5 molecules of water, $\Delta m_{calcd}/m = 2.20$ %) per formula unit.

Considerable interest in microporous borophosphates has been paid due to their potential applications in sorption. The sorption property of **1** has been investigated by dipping the as-synthesized sample of **1** (50 mg) in 100 mL methanol under stirring for 7 days. Then the resulting sample was washed repeatedly with deionized water and then air-dried at room temperature. The result indicates that methanol molecules could not be adsorbed by IR spectral examination.

Direct-current magnetic susceptibility studies of **1** have been carried out in an applied magnetic field of 1000 Oe in the temperature range 2-300 K (Fig. 3). The plot of X_MT versus T, in which X_M is the molar magnetic susceptibility, is shown in Fig. 5. At 300 K, the X_MT value of 1.04 cm^3 K mol^{-1} is very close to the expected value of 1.12 cm^3 K mol^{-1} ($S = 1/2$, $g = 2$). The X_MT product gradually reaches to a maximum of 10.72 cm^3 K mol^{-1} at about 2 K as the temperature decrease, which obviously suggests the presence of intra-molecular ferromagnetic interactions in **1**.
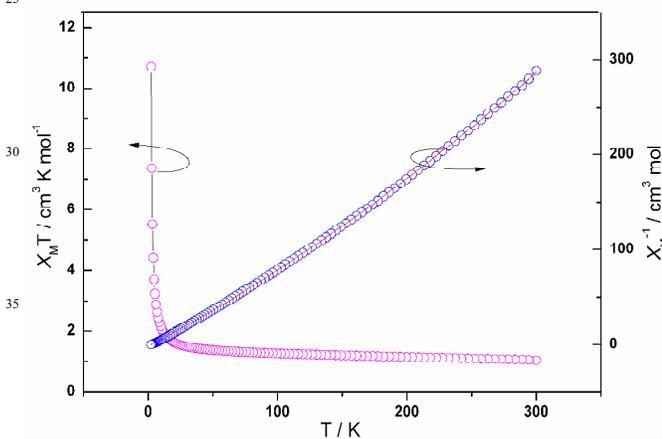

Figure 3. The magnetic property of compound **1**.

The catalytic activity of **1** for the oxidative degradation of chitosan based on H$_2$O$_2$ technology in heterogeneous phase was studied. The results of the contrast degradation test[14] were shown in Fig. 4a. The degradation ratio of chitosan was confirmed according to:

$$R\ (\%) = (M_0 + M_c + M_x)\ /M_0 \times 100\ \%.$$

Where R refers to degradation ratio, M_0, M_c refers to the quantity of original chitosan and borophosphate, respectively. M_x refers to the quantity of collected solid after degradation of different conditions. The results showed that chitosan can not be degradated under the catalysis of copper borophosphate without H$_2$O$_2$. The degradation ratio was 29 % only using H$_2$O$_2$ without catalyst, which indicated that H$_2$O$_2$ was used alone, the yield of free radicals formed by decomposing of H$_2$O$_2$ was rather slow and could not efficiently attack the β-D-(1→4) glucosidic linkages of chitosan. But in the presence of **1**, chitosan could be degraded effectively with degradation ratio of 100 %. Therefore,

it can be predicated that **1** is an excellent catalyst for oxidative degradation of chitosan with H$_2$O$_2$ in heterogeneous phase. Under the catalysis of **1** for different duration,[15] chitosan was degraded heterogeneously with H$_2$O$_2$ into water-soluble low molecular weight chitosan. Effect of reaction time on viscosity-average molecular weight (Mv) of chitosan degraded was shown in Fig. 4b. The results showed that Mv of chitosan dropped sharply from 210, 000 to 8300 within 60 min. In the heterogeneous phase, the degradation mechanism may be related to the borophosphate anion [B$_6$P$_9$O$_{33}$(OH)$_3$]$^{12-}$. The anion would react with H$_2$O$_2$ continually and produced a great number of free radicals, which can quickly attack the β-D-(1→4) glycosidic bonds of chitosan and subsequently broke the glycosidic linkages.
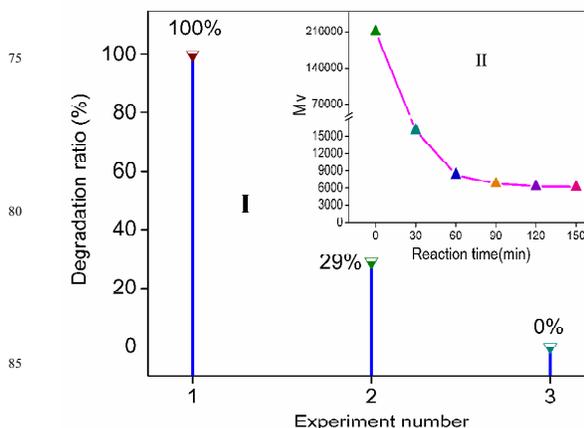

Figure 4. (a) The contrast of degradation ratio under different conditions. (b) Effect of reaction time on Mv of low molecular weight chitosan.

In summary, the novel open-framework copper borophosphate with 1-D (4, 4)-connected borophosphate anion has been synthesized by using boric acid flux method. Magnetic measurements indicate that **1** exits ferromagnetic interactions. It is the first example to investigate the catalytic activity for the oxidative degradation of chitosan in the series of borophosphates. The high catalytic activities indicate that **1** may be applicable as an excellent heterogeneous catalyst. The compound enriches the family of borophosphates, and it will provide an impetus for searching for new functional materials with high catalytic activity.

Acknowledgements

Notes and references

‡ Compound **1** was synthesized from a mixture of H$_3$BO$_3$, Na$_2$HPO$_4$·12H$_2$O, CuAC$_2$·H$_2$O and KF·2H$_2$O in a molar ratio of 16: 1: 2: 1.5 by means of boric acid flux method. The mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 200 °C for 7 days. After the mixture was slowly cooled to room temperature, green polyhedral crystals suitable for X-ray structure determination were obtained. The attempts to prepare the **1** analog using other boron sources (such as B$_2$O$_3$ and Na$_2$B$_4$O$_7$·10H$_2$O) and phosphorus source (85 *wt* % H$_3$PO$_4$) were unsuccessful up to the present.

§ Structure Determination: The data for the crystal (0.26 × 0.18 × 0.16 mm) were collected on a Bruker APEX-II CCD diffractometer (Mo-Kα, λ =0.71073 Å) at 296(2) K. A total of 8202 reflections were collected, of which 1040 reflections were unique (R_{int} = 0.0798). The structure was [5] solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software. The hydrogen atoms attached to protonated O(4) atoms and water molecules O1W were not added. All the non-hydrogen atoms were refined anisotropically. In the crystal structure, the Na(2) and Na(3) sites are disordered which were freely refined site-[10] occupation factors in the ratio 0.5: 0.5 (1: 1). Crystal data (CSD: 426408): B$_9$Cu$_3$H$_5$KNa$_5$O$_{37}$P$_6$, hexagonal, space group $P6_3/m$ (no. 176), $a = b =$ 11.574(4) Å, $c = 12.361(4)$ Å, $V = 1433.9(9)$ Å^3, Z =2, D_c = 2.825 g/cm^{-3}, μ = 2.914 mm^{-1}, $F(000)$ = 1184, GOF = 1.051, R_1 = 0.0525 and wR_2 = 0.1253 ($I > 2\sigma(I)$).

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14. The contrast degradation test: for each experiment, 1.0000 g chitosan with a degree of deacetylation of 98.36 % and Mv of 210,000 was [75] placed in a 200 mL conical flask and soaked thoroughly after adding 100 mL distilled water. Then 0.0100 g compound **1** was added into the conical flask for experiment 1, after adding 2.0 mL 30 % (*wt* %) H$_2$O$_2$ aqueous solutions, the oxidation degradation of chitosan was carried out at 70 °C for 30 min. But catalyst was not used for [80] experiment 2, and H$_2$O$_2$ was not used for experiment 3.
15. The heterogeneous degradation test for different duration: 1.0000 g chitosan with a degree of deacetylation of 98.36 % and Mv of 210,000 was put into 200 mL conical flask, then 0.0100 g borophosphate, 100 mL distilled water, 2.0 mL 30% (*wt* %) H$_2$O$_2$ [85] aqueous solutions were also added. The solution was stirred and reacted at 70 °C for 30, 60, 90, 120, 150 min. The viscosity-average molecular weight (Mv) of degraded chitosan was determined by viscosity measurements.

Graphical Abstract

The compound can be viewed as a 3-D open framework constructed by the connection of $Cu^{II}O_6$ octahedra and 1-D (4, 4)-connected borophosphate anionic structure composed of trigonal-planar $BO_2(OH)$ groups, tetrahedral BO_4 and PO_4 groups. It not only features novel borophosphate anionic partial structure containing 1-D 12-MR channels, but also exhibits ferromagnetic interactions and high catalytic activity for oxidative degradation of chitosan.