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A Novel Open-Framework Copper Borophosphate: $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$

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A new open-framework copper borophosphate was hydrothermally synthesized and structurally characterized. Its structure may be regarded as a layer forming via vertex-sharing $BO_3(OH)$ and PO_4 tetrahedra bonded together with $CuO_2(OH)_2(H_2O)_2$ octahedral units. The thermal stability and magnetic properties are also discussed.

The simple borates and phosphates, such as BBO(β-BaB_2O_4),[1] LBO(LiB_3O_5),[2] KTP($KTiOPO_4$),[3] and KDP-(KH_2PO_4),[4,5] are most of the best known materials with optical, electrooptical, and ferroelectric applications and are well-known commercially and industrially for making a range of different optical elements. Boron phosphates possess excellent catalytic activity in some chemical synthesis and have been used as catalysts in the chemical industry.[6] Moreover, the basic building blocks of these borates (BO_3 and BO_4) and phosphates (PO_4) are similar to the primary building units of the natural and artificial polyporous materials such as silicates (SiO_4), aluminosilicates (AlO_4 and SiO_4), and aluminophosphates (AlO_4 and PO_4), which have been extensively applied in the areas of ionic exchange, absorption, separation, and catalysis. These phenomena have allowed chemists to pursue the designed preparation of the borophosphate materials with defined architecture and useful chemophysical properties because it has long been anticipated that suitably designed multimetallic complexes could provide distinct reactivity patterns different from those shown by analogous monometallic systems.[7] Such effort has been made in the last few years. The numerous borophosphates and their crystal structures have already been reported.[8,9] Sevov reported the first zeolite-like borophosphate, $CoB_2P_3O_{12}OH \cdot C_2H_{10}N_2$, with an infinite framework.[10] Kniep et al. first reported transition-metal borophosphates, $M^IM^{II}(H_2O)_2[BP_2O_8] \cdot H_2O$ (M^I = Na, K; M^{II} = Mg, Mn, Fe, Co, Ni, Zn), which contain 6_1 helices from tetrahedral ribbon,[11] and then proposed a first approach to borophosphate structural chemistry.[9] Up to the present, the structural chemistry of borophosphate anions has extended from isolated species, oligomers, rings, chains, and layers to the three-dimensional open frameworks. In our experiment, we combine a metal phosphate system with boron to encounter several such interesting materials. In particular, we discovered an open-framework copper borophosphate. Its structure may be regarded as a layer forming via vertex-sharing $BO_3(OH)$ and PO_4 tetrahedra bonded together with $CuO_2(OH)_2(H_2O)_2$ octahedral units. In this Communication, we describe the synthesis and structure of this novel material, **I**, of the

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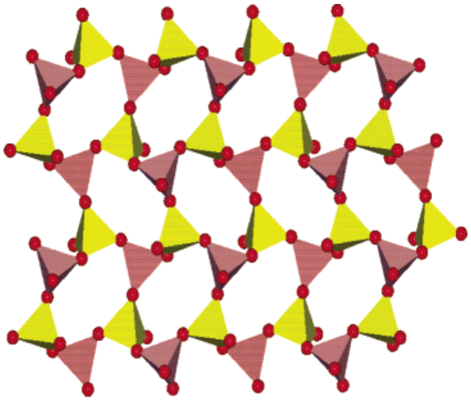

Figure 1. Connectivity of polyhedra in the *bc* plane.

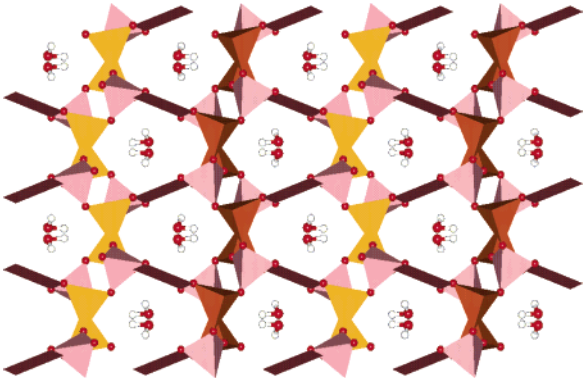

Figure 2. Framework along the (001) direction showing the pear-shaped eight-ring channel in the compound.

composition $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$, exhibiting thermal properties and ferrimagnetic interactions.

Compound **I** was synthesized by heating a mixture of $Cu(CH_3COO)_2 \cdot H_2O$, H_3BO_3, H_3PO_4 (85 wt %), and H_2O in a molar ratio of 1:2:3:11 at 110 °C for 3 days in a sealed thick walled Pyrex tube. The blue polyhedral crystal yield of 60% based on Cu was obtained and structurally characterized by single-crystal X-ray diffraction.[12] The crystal structure of the title compound is well-ordered, and three H atoms were located in difference Fourier maps: two H atoms belong to the water molecule (O6), while the other one is attached to O5 in the boron−oxygen polyhedron $[BO_3(OH)]$. The basal building blocks, $BO_3(OH)$ and PO_4, exhibit the almost regular tetrahedron configuration. The B−O distances and O−B−O angles range from 1.452 to 1.469 Å and from 106.7 to 111.4° for the $BO_3(OH)$. The interatomic distances and O−P−O angles in the PO_4 tetrahedra range from 1.497 to 1.542 Å and from 103.9 to 114.4°, respectively. A whole crystal structure can be regarded as an open-framework structure containing a three-dimensional intersecting system of different types of channels, running along *a*, *b*, and *c* axis directions. In this case, the condensation of the strictly alternating $BO_3(OH)$ and PO_4 tetrahedra through common vertexes comprises the six-membered rings of the tetrahedra, on the other hand, in which each tetrahedron $[BO_3(OH)$ or $PO_4]$ is shared with another two neighboring such six-membered rings of the tetrahedra around it, and, in such way, finally leads to the infinite two-dimensional extension structure or the infinite two-dimensional layer building up from borophosphate anions (see Figure 1). In this layer, each $BO_3(OH)$ or PO_4 tetrahedron with one free vertex simultaneously belongs to three adjacent six-membered rings of the tetrahedra. These six-membered rings show a slightly distorted chair configuration. Two different configurations of the six-membered rings can be distinguished in *UUUUDD* and *UUDDDD* conformations in the layer, respectively. Neighboring layers are interconnected by Cu^{2+} acting as a linker to form an infinite three-dimensional open-framework structure (Figure 2).

The coordination environment of Cu^{2+} is very interesting. It may be looked upon as a square-planar configuration involving two trans oxygens from the PO_4 groups and two trans hydroxos from the $BO_3(OH)$ groups in the six-membered rings of two adjacent layers with Cu−O distances ranging between 1.943 and 1.954 Å (Figure 2) and may also be looked upon as a severe distortion octahedral coordination involving two trans aqua ligands with Cu−O distances of 2.532 Å except for the four oxygen species mentioned above. The results of the bond valence sum (BVS) analysis[13] imply that the square-planar configuration seemed to be more reasonable than the octahedral coordination configuration, because the +1.94 oxidation state of the copper atom in the square-planar configuration and the 2.14 value in the octahedral coordination configuration with two trans aqua ligand coordination were given by the BVS calculation. However, by IR spectral examination, such waters in the channels (Figure 2) first, middle, and last cannot be exchanged after the prepared powder sample of $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$ was dipped in methanol for 72 h at room temperature. It hints that weak interaction occurred between the Cu^{2+} and water molecules. On the basis of this fact, the coordination geometry of Cu^{2+} may be recognized as the octahedral coordination, however, in which the Cu^{2+}−Ow (Ow: oxygen atom in the water molecule) distance is 0.201 Å longer than the longest Cu^{2+}−O bond length reported in the literature $[Cu(C_2H_{10}N_2)][B_2P_3O_{12}(OH)]$:[14] Cu−O = 1.963−2.331 Å]. Such a severe distortion octahedron $CuO_2(OH)_2(H_2O)_2$ is unprecedented.

The Cu atoms located in the middle between the borophosphate anion layers, by connection with four oxygen atoms from the $BO_3(OH)$ or PO_4 tetrahedra in the adjacent different layers, result in another interesting phenomenon,

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(12) The data for the crystals (0.49 mm × 0.30 mm × 0.39 mm) were collected on a Rigaku Mercury CCD area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data were collected at a temperature of −80 °C to a maximum 2θ value of 55.0°. A total of 6686 reflections were collected, of which 952 reflections were unique ($R_{int} = 0.067$). The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The full-matrix least-squares refinement on F^2 was based on 937 observed reflections and 92 variable parameters. Crystal data for $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$: $M = 345.16$, space group *Pbca*, $a = 13.487(7)$ Å, $b = 8.331(4)$ Å, $c = 7.827(4)$ Å, $Z = 4$, $D_c = 2.607$ g/cm^3, $\mu = 2.914$ mm^{-1}, $V = 879.4(7)$ Å^3, R1 = 0.028, wR2 = 0.099, GOF = 1.01 for 937 observed reflections with $I > 2.0\sigma(I)$.

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i.e., a conformation of the neutral open framework with one-dimensional pear-type channels running along the *c* direction of the orthorhombic unit cell (see Figure 2). This structure is a distinct difference from the open framework with negative charge in the zeolite-like borophosphate, $CoB_2P_3O_{12}OH \cdot C_2H_{10}N_2$.[10] The channels in the crystal structure are formed from eight polyhedra sharing vertexes in the following sequence: $-CuO_6-BO_4-PO_4-BO_4-PO_4-CuO_6-BO_4-PO_4-$. The short axis of the channel is about 5.72 Å, and the long axis is about 6.62 Å. Further cross-linking occurs via hydrogen-bond interactions between Cu-bonded aqua ligands and $[B_3P_3O_{12}(OH)_3]^{3-}$ rings [Ow···O(5) = 2.720(2) Å; Ow···O(2) = 2.959(3) Å; Ow···O(4) = 3.012(2) Å].

It also is significant to compare the network structure of **I** containing a weak interaction of the Cu^{2+}-centered and water molecules (as shown in Figure 2) with the structurally known zeolite or molecular sieve. The wide framework variation, once again, exemplifies the versatility of the transition-metal borphosphate structure, as similar as that founded in a vast number of open-framework aluminosilicate zeolite and aluminophosphate molecular sieves.[15−17] The anion layer of the framework in the crystal of $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$ is essentially identical with the structure of the tetrahedral layer in the solid aluminosilicate materials $NaAlSiO_4$, in which the six-membered rings are built up by regularly alternating AlO_4 and SiO_4 tetrahedra by sharing corners.[18] These results suggest that the copper borophosphate $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$ with a naked active metal center not only maybe provides a rich structural chemistry of borophosphates but also likely possesses unanticipated technological applications such as absorption, separation, and catalysis.

Thermal dehydration of $Cu(H_2O)_2[B_2P_2O_8(OH)_2]$ was run over two distinct stages. The weight loss of 10.6% (calcd 10.4%) at the first step was observed from 125 to 260 °C and corresponds to the two coordinated water molecules. At the second step, a gradual loss of 4.1% (calcd 4.2%) from 320 to 500 °C was attributed to the loss of 2 mol of hydroxyl groups. Powder X-ray diffraction analysis indicated that the recovery of the hydration phase was not obtained by exposing the sample of the dehydration phase after the first dehydration step to moist air for 24 h, which is different from the characterization of reversible dehydration/rehydration for $NaZn(H_2O)_2BP_2O_8 \cdot H_2O$.[19] Investigation of phase changes between 50 and 850 °C showed that the sample was still crystalline below 300 °C, then became amorphous between 300 and 500 °C, and above 600 °C formed a new phase.

The temperature-dependent molar magnetic susceptibility of the title compound in the temperature range of 80−320 K shows that the change of the molar magnetic susceptibility with decreasing temperature increases and reaches up to a maximum value at about 105 K, indicating a typical ferrimagnetic interaction ($\Theta = 27.77$). The effective magnetic moment derived from experimental measurement at 300 K, $1.64\mu_B$, is slightly lower than that expected for spin-only measurement with $S = {}^1/_2$ ($\mu_{eff} = 1.73\ \mu_B$).

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Supporting Information Available: Crystallographic data for this compound in CIF format and figures of its in situ X-ray diffraction, thermal analysis, and magnetic properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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