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Novel Coordination Polymer Containing a Mixed Valence Copper(I,II) Phosphonate Unit: $Cu^{I}_2Cu^{II}(hedpH_2)_2(4,4'\text{-}bpy)_2 \cdot 2H_2O$ (hedp = 1-Hydroxyethylidenediphosphonate)

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This paper reports the synthesis and crystal structure of a novel mixed valence copper(I,II) compound, $Cu^{I}_2Cu^{II}(hedpH_2)_2(4,4'\text{-}bpy)_2 \cdot 2H_2O$ (**1**), where hedp represents 1-hydroxyethylidenediphosphonate. The structure is composed of $\{Cu^{I}_2Cu^{II}(hedpH_2)_2\}$ trimer units and 4,4′-bipyridine linkages, forming a two-dimensional brick-wall-like layer structure in the *ab* plane. The layers are stacked along the [001] direction with strong interlayer hydrogen bonds and $\pi-\pi$ interactions, thus leading to the construction of a three-dimensional network.

A number of metal phosphonate compounds have been prepared in the past decades because of their potential important applications in exchange, absorption, and sensors.[1−6] Among these, compounds with open framework or porous structures are of special interest. It was found that pores in some phosphonate compounds were expanded after introducing a second inorganic species such as phosphate or phosphite.[7,8] Although a few phosphonate compounds containing terminal organic ligands were reported recently,[9] exploration of those involving a second organic bridging ligand is rare, despite the current intense interest in searching for stable microporous coordination networks as organic analogues of zeolites.[10] Our efforts along this line have resulted in a three-dimensional copper phosphonate $Cu_4(hedp)_2(pz)(H_2O)_4$,[11] where pyrazine (pz) bridges the $\{Cu_4(hedp)_2(H_2O)_2\}$ layers [hedp = 1-hydroxyethylidenediphosphonate, $CH_3C(OH)(PO_3)_2^{4-}$]. In this paper, we describe the synthesis and crystal structure of a novel mixed valence copper(I,II) compound $Cu^{I}_2Cu^{II}(hedpH_2)_2(4,4'\text{-}bpy)_2 \cdot 2H_2O$ (**1**) in which the molecular trimer units of mixed valence copper phosphonate are linked by rodlike 4,4′-bipyridine (4,4′-bpy) into a unique layer structure.

The hydrothermal treatment of a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.2421 g, 1 mmol), 50% $hedpH_4$ (2.5 mmol, 1 mL), 4,4′-bpy (0.1540 g, 1 mmol), and H_2O (4 mL), adjusted by an aqueous solution of NaOH (1 M) to pH = 1.76, at 165 °C for 2 days, resulted in the formation of yellow platelike crystals of the title compound as a major phase.[12] A small amount of unidentified yellow powder appeared as a minor phase. The crystals were manually selected for structure determination and the measurement of bulk properties. The XPS spectrum of the bulk sample showed the shoulder peaks

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(12) Anal. Calcd for $C_{24}H_{32}Cu_3N_4O_{16}P_4$: C, 30.44; H, 3.41; N, 5.92. Found: C, 32.04; H, 4.11; N, 5.85%.

10.1021/ic015631o CCC: $22.00

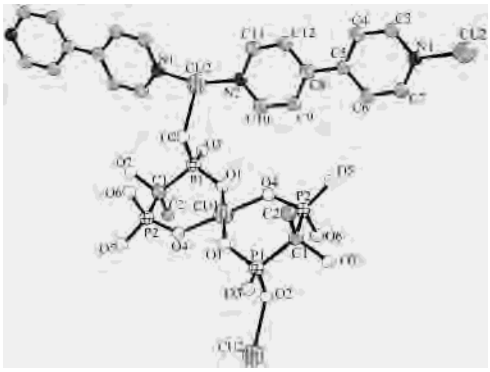

Figure 1. T-shaped building unit of structure **1** with the atomic labeling scheme.

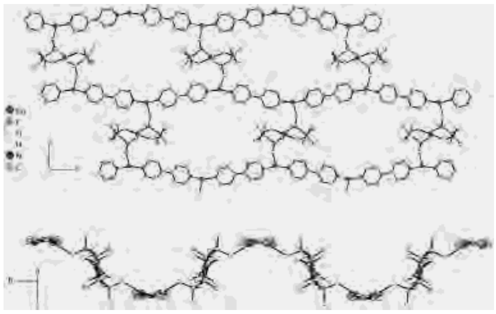

Figure 2. One layer of structure **1** along the [001] direction (top) and the [102] direction (bottom).

of $^2P_{3/2}$ and $^2P_{1/2}$ at 934.7 and 954.1 eV, respectively, suggesting the presence of Cu^I in the compound. The evident satellite peaks at 943.6 and 962.9 eV indicated that the compound also contains Cu^{II} ions.

Single-crystal X-ray diffraction measurement[13] revealed a two-dimensional brick-wall-like layer structure, composed of $\{Cu^I_2Cu^{II}(hedpH_2)_2\}$ trimer units and 4,4′-bipyridine linkages (Figures 1 and 2). Two independent Cu atoms are found in the trimer unit and are bridged by $hedpH_2^{2-}$ ligands. The calculated bond valence sums[14] are 1.85 for Cu(1) and 1.01 for Cu(2), respectively. The divalent Cu(1) atom has an approximate square planar geometry, with the four biting sites provided by pairs of the phosphonate oxygens [O(1), O(4)] from two equivalent $hedpH_2^{2-}$ groups. The Cu(1)−O bond lengths are 1.927(3) and 2.008(3) Å. The monovalent Cu(2) atom is trigonal planar in coordination and is coordinated to one phosphonate oxygen [O(2)] and two nitrogen atoms [N(1), N(2)] from equivalent 4,4′-bipyridine ligands. The Cu(2)−O(2) distance [2.237(3) Å] is slightly longer than those of Cu(2)−N [1.914(3), 1.923(4) Å]. The Cu(2) atoms of each trimer are connected by bifunctional 4,4′-bipyridine ligand, forming T-shaped building units as shown in Figure 1. The N(1)−Cu(2)−N(2) bond angle is 158.8(1)°. These units are repeated in the *ab* plane, forming a brick-wall-like layer with zigzag fluctuation (Figure 2). The layers are stacked along the [001] direction with interlayer $\pi-\pi$ interactions between the pyridine rings[15] (Figure 3). The average centroid−centroid contact between two pyridine fragments from the adjacent layers is 3.729 Å, and the average interplane angle is 11.6°. Strong interlayer hydrogen bonds exist between the phosphonate oxygens [O(1), O(3), O(5), O(6), and O(7)] as well as the hydroxy oxygen O(7), forming a hydrogen bonded copper phosphonate layer $\{Cu^{II}(hedpH_2)_2\}$ in the *ac* plane. The O(3) and O(6) atoms are protonated [P(1)−O(3) 1.562(3) Å, P(2)−O(6) 1.559(3) Å]. The shortest O···O contact is 2.531(4) Å for O(6)···O(5). Therefore, a three-dimensional network is constructed.

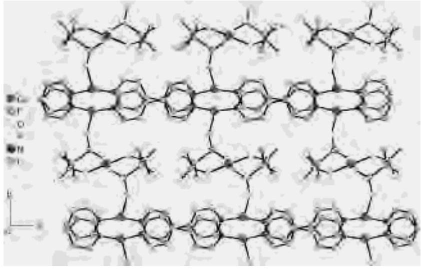

Figure 3. Packing diagram of structure **1** along the [001] direction.

Compound **1** is unique in three aspects. First, it contains trimer units of mixed valence copper(I,II) phosphonate $\{Cu^I_2Cu^{II}(hedpH_2)_2\}$, separated by 4,4′-bipyridine linkages. Although numerous work has been devoted to the molecular complexes with mixed valence copper(I/II) because of biological interest,[16,17] few studies are concerned with extended solids.[18] As far as we are aware, there is only one example of mixed valence copper phosphonate, $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$, which shows an open framework structure.[19] Unlike $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$, however, compound **1** is not air-stable especially in a wet atmosphere, as indicated by its color change from yellow to green. The XPS spectrum of the green material showed satellite peaks at 947.2 and 966.4 eV, and no shoulder peaks of $^2P_{3/2}$ and $^2P_{1/2}$ were observed. Second, compound **1** contains trigonal planar Cu(I) in the structure. Such a coordination mode is uncommon in the coordination polymers of copper.[20] The stabilization of three-coordinate copper(I) in the title compound could be due to the interlayer $\pi-\pi$ stacking interactions between coordinated 4,4′-bipyridine molecules.[21] The trigonal planar

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(13) Crystal data for **1**: $C_{24}H_{32}Cu_3N_4O_{16}P_4$, $M_r = 947.04$, monoclinic, space group $P2_1/c$, $a = 10.206(2)$ Å, $b = 21.400(4)$ Å, $c = 7.306(2)$ Å, $\beta = 91.17(3)°$, $V = 1595.2(6)$ Å^3, $Z = 2$, $D_c = 1.972$ g cm^{-3}, μ(Mo Kα) = 22.66 cm^{-1}, $\lambda = 0.71073$ Å. A crystal of dimensions 0.20 × 0.15 × 0.02 mm^3 was selected for indexing and intensity data collection at 298 K, using a Siemens SMART CCD system. Total number of measured and observed independent reflections ($I_0 > 2\sigma(I)$) are 8332, 2900 ($R_{int} = 0.0647$). Least-squares refinements were based on F^2 and converged at R1 = 0.0438, wR2 = 0.0939, GOF = 0.936.

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Cu(I) also resulted in an approximately T-shaped building unit and, further, a brick-wall-like layer. A few other structurally distinct compounds with T-shaped moieties have been reported, some of which give large pores.[10d,22] In the present case, although large windows are observed in a single layer of the structure, the stacking mode of the layers reduces the channel size remarkably. Third, it is worth noting that the two CPO_3 groups of each $hedpH_2^{2-}$ ligand show different coordination modes in the title compound. One is linked to one copper atom [Cu(1)], and the other, to two copper atoms [Cu(1) and Cu(2)]. The methylenic carbon C(1) is consequently chiral, and racemic phosphonate blocks are observed within the $Cu^{II}(hedpH_2)_2$ unit.

In summary, the combination of a molecular phosphonate unit with a second organic bridging ligand leads to a novel neutral compound, $Cu^{I}_2Cu^{II}(hedpH_2)_2(4,4'\text{-bpy})_2\cdot 2H_2O$ (**1**). The compound has a two-dimensional brick-wall-like structure with strong interlayer hydrogen bond interactions and $\pi-\pi$ interactions. This work demonstrates that novel coordination polymers with open framework are feasible by introducing a second bifunctional organic ligand into the metal phosphonate units.

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Supporting Information Available: Crystallographic file in CIF format. Figures in PDF. This material is available free of charge via the Internet at http://pubs.acs.org.

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