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An interesting fourfold interpenetrating network constructed by polyoxometalates and metal–organic coordination complexes: $[Cu^{I}_{5}(bpy)_{5}(H_2O)_2][[Cu^{II}(H_2O)_3]_2Cu^{II}[P_4Mo^{V}{}_6O_{25}(OH)_6]_2]\cdot H_3O^+\cdot 2H_2O$

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Abstract

A novel fourfold interpenetrating 3D network compound, $[Cu^{I}_{5}(bpy)_5(H_2O)_2][[Cu^{II}(H_2O)_3]_2Cu^{II}[P_4Mo^{V}_{6}O_{25}(OH)_6]_2]\cdot H_3O^+\cdot 2H_2O$ **1** (bpy = 4,4′-bipyridine), has been synthesized and characterized by elemental analyses, IR, TG analyses, and single-crystal X-ray diffraction. Compound **1** is built up of $Cu[P_4Mo_6O_{25}(OH)_6]_2$ clusters covalently linked by Cu-bpy coordination polymer chains to yield unusual two-dimensional layers, which are further connected together by metal coppers to produce an interesting fourfold interpenetrating 3D network structure. The crystal data for compounds **1**: Triclinic, space group $P\bar{1}$, $a = 12.714(3)$ Å, $b = 14.882(3)$ Å, $c = 15.369(3)$ Å, $\alpha = 72.74(3)°$, $\beta = 72.12(3)°$, $\gamma = 65.62(3)°$, $V = 2471.9(9)$ Å^3, $Z = 1$.

Keywords: Interpenetrating network; Polyoxometalates; Copper–organic complexes; Hydrothermal synthesis

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1. Introduction

Entangled systems, one of the major themes of supramolecular chemistry, are common in biology – as seen in catenanes, rotaxanes, and molecular knots [1] and have attracted considerable attention due to their aesthetic and often complicated architectures and topologies [2]. Interpenetration has been the most investigated type of entanglement, as shown by the two comprehensive reviews by Batten and Robson [3]. More recently, a complete analysis of all the 3D interpenetrating structures contained in the CSD database was also carried out with a rationalization and classification of the topology of the interpenetration [4]. Once rare, these are now becoming increasingly common and many complex type of entanglement being recognized [5]. However, interpenetrating compounds, constructed by metal–organic coordination complexes and polyoxometalates, remain largely unexplored [6]. Polyoxometalates (POMs), as anionic early-transition-metal oxide clusters, bear many properties that make them attractive for applications in different areas such as catalysis, biology, magnetism, optics, and medicine [7]. Because of the remarkable features of metal oxide surfaces and their diversities in geometric topology, polyoxometalates have been employed as inorganic building blocks for the construction of larger cluster, or one-, two-, and even three-dimensional (3D) extended solid frameworks [8–12]. However, the preparation of high-dimensional interpenetrating structures based on POM building blocks and metal–organic coordination complexes has not been extensively studied. Therefore, the search for suitable organic molecules, metal cations, and POM building blocks to be applied in the construction of high-dimensional interpenetrating structures is one of the most challenging issues in synthetic chemistry and material science.

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In an attempt to construct 3D interpenetrating structures, we chose the 4,4′-bpy based on the following considerations: (1) it can act as a bidentate ligand to bridge metals, forming variously novel structures. Such as porous structures [13] and interpenetrating structures [14]. (2) Generally, longer ligand will lead to larger voids. In a very loose and general sense it can be said that the larger the voids in a 3D net the more likely interpenetration occurs and the more number of independent nets a particular void is passed through. In transition metals, the copper possesses many particular characteristics. For instance, copper has two kinds of valences: +1 and +2, generally, Cu^{1+} has two, three and four coordination environment and Cu^{2+} has four, five and six coordination environment. If there are the mixed-valence cupper species in the compounds, the metal copper will form variously interest structures. In this field, Chen group have synthesized many novel compounds by adopting the hydrothermal method [15].

In the field of POMs, reduced molybdenum phosphates constitute a large class of compounds and received much attention for their applications in catalysis, ion exchange, and molecular sieves [16]. The $[P_4Mo_6O_{25}(OH)_6]^{6-}$ anion (denoted $[P_4Mo_6O_{31}]^{12-}$), with various degrees of protonation is the most often encountered building unit in the reduced molybdenum phosphates because of the relatively small volume and the abundant terminal oxygen atoms. Our group and others have synthesized some reduced molybdenum phosphates with $[P_4Mo_6O_{31}]^{12-}$ as basic building block ranging from one-dimensional polymers [17] to two- [18] and three-dimensional [19] microporous or tunnel materials. In these reported work, $[P_4Mo_6O_{31}]^{12-}$ polyanions were all synthesized by the hydrothermal method. Although $[P_4Mo_6O_{31}]^{12-}$ is a familiar polyanion in POMs, whose characters of relatively small volume and the abundant terminal oxygen atoms may provide the probability that transition metal complexes covalently bond to the $[P_4Mo_6O_{31}]^{12-}$ building blocks to form the 3D interpenetrating structures.

In view of these, fortunately, by trial and error we have now synthesized a new compound by adopting the hydrothermal method, $[Cu^I_5(bpy)_5(H_2O)_2][[Cu^{II}(H_2O)_3]_2Cu^{II}[P_4Mo^V_6O_{25}(OH)_6]_2]\cdot H_3O^+\cdot 2H_2O$ **1**, exhibiting a novel fourfold interpenetrating 3D network structure, according to the aforementioned idea.

2. Experimetal section

2.1. Materials and methods

All chemicals purchased were of reagent grade and were used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Mo, Cu and P were determined with a Leaman inductively coupled plasma (ICP) spectrometer. The FTIR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer as pressed KBr pellets. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 at a heating rate of 10 °C min^{-1}.

2.2. Syntheses

In a typical synthesis of compound **1**, $CuCl_2\cdot 2H_2O$ (0.6 mmol), Mo (0.15 mmol) and 4,4′-bpy (0.3 mmol) were added to a stirred solution of $Na_2MoO_4\cdot 2H_2O$ (0.3 mmol) and H_3PO_4 (1.2 mmol) in water (9 mL). The resultant mixture was sealed in a 23-mL, Teflon-lined autoclave and heated at 160 °C for 5 d. The final pH value was ca. 4.1. Red, block-like crystals of **1** were obtained from the solid product in a yield of 20% (based on Mo). Anal. Calc. for $C_{50}H_{75}P_8Cu_8 Mo_{12}N_{10}O_{73}$ (3891.56): C, 15.43; H, 1.92; Cu, 13.07; Mo, 29.59; N, 3.60; P, 6.37. Found: C, 15.18; H, 2.28; Cu, 12.75; Mo, 29.26; N, 3.88; P, 6.59.

2.3. X-ray crystallography

A red single crystal of compound **1** was carefully selected under a polarizing microscope and severally glued on a glass fiber. The data of X-ray diffraction were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) operating at 293 K in the range of $3.02 < \theta < 25.50$ °. Empirical absorption correction was applied. A total of 20,546 (9146 unique, $R_{int} = 0.0337$) reflections were measured ($-15 \leqslant h \leqslant 15$, $-18 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 18$).

The structure of compound **1** was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL97 software [20]. All the non-hydrogen atoms in **1** were refined anisotropically, in **1** positions of the hydrogen atoms attached to nitrogen atoms and those to carton atoms were fixed in ideal positions, and other hydrogen atoms were not located. A summary of the crystallographic data and structural determination for **1** is provided in Table 1. Selected bond lengths and bond angles of **1** are listed in Table 2. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of **1** are available in supplementary crystallographic data.

CCDC reference number: (631162) for **1**.

3. Results and discussion

3.1. Structrue description

Single-crystal X-ray diffraction reveals that **1** has a novel fourfold interpenetrating network structure consisting of four equivalent 3D interwoven nets. For a single net, it is built from $[P_4Mo_6O_{25}(OH)_6]^{6-}$ polyoxoanions, Cu ions, 4,4′-bpy organic molecules, and the water molecules. $[P_4Mo_6O_{31}]^{12-}$ is made up of six MoO_6 octahedra and four PO_4 tetrahedra (see Fig. S1 left). Each $[MoO_6]$ unit has a terminal oxygen atom and shares two edges with neighboring $[MoO_6]$ octahedral. Six $[MoO_6]$ octahedra are coplanar and constitute a hexametric molybdenum cluster with