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Three-dimensional supramolecular networks constructed from Keggin anions and metal–organic complex with unpredicted oxidation of an N-heterocycle ligand

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ABSTRACT

Two novel Keggin polyoxometalate compounds, $[Cu_2(PCA)_4(H_2O)_2][SiW_{12}O_{40}]\cdot 8H_2O$ (**1**) and $[Cu(PCA)_2(H_2O)_4][Cu(PCA)_3(H_2O)][SiW_{12}O_{40}]\cdot H_2O$ (**2**) (PCA = pyridine-4-carboxylic acid), were synthesized by in situ generation of pyridine-4-carboxylic acid ligand from 1,3-bis(4-pyridyl)propane precursor under hydrothermal conditions. Compounds **1** and **2** were structurally characterized by elemental analysis, IR and UV spectrography, TGA and single-crystal X-ray diffraction analysis. The variable-temperature magnetic susceptibility was measured at 2–300 K for **1**. The compound **1** consists of polyoxoanions $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$, dimer cations $[Cu_2(PCA)_4(H_2O)_2]^{4+}$ and lattice water molecules. The water molecules link $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ and $[Cu_2(PCA)_4(H_2O)_2]^{4+}$ into three-dimensional (3D) architecture *via* hydrogen bonds. Polyoxoanions of **2** are linked into 1D chains through hydrogen bonds. Moreover, 1D chains are further extended into 3D supramolecular networks by hydrogen bonds and $\pi\cdots\pi$ stacking interactions of pyridine-4-carboxylic acid molecules. The variable-temperature magnetic measurement of **1** shows an antiferromagnetic interaction in the 2–300 K temperature range.

1. Introduction

Polyoxometalates (POMs), as an abundant class of metal-oxide cluster compounds, have been found applications in a wide range of fields, including molecular magnetism [1], catalysis [2], and medicine [3]. The study on POMs has been attracting a lot of attention of chemists worldwide. Because POMs have high charge density and the active terminal oxygen and bridging oxygen atoms on the surface as electron and proton reservoirs, supramolecular compounds based on POM are possible prone to be synthesized. Recently, extensive efforts have been devoted to synthesizing supramolecular compounds and a few 1D, 2D and 3D supramolecules were obtained under appropriate reaction conditions [4].

On the other hand, recent studies have proved the hydrothermal synthesis to be an effective method for in situ ligand synthesis. It provides an opportunity to generate organic ligands that are difficult to be synthesized in a conventional method [5]. This strategy was tested and completed successfully. For example Ming-Liang Tong and co-workers have been researching a few metal/organic reactions such as ligand oxidative coupling, hydrolysis, and substitution under hydrothermally conditions [6]. They have observed the simultaneous dehydrogenative coupling and hydroxylation of an N-heterocyclic ligand bpp to produce a new ligand chtpy (chtpy = a,a-1, 4-dihydroxy-e,e,e,e-1,2,4,5-tetra(4-pyridyl)cyclohexane) for the first time [7]. Whereas, Wang's research group has also obtained the complicated organic ligand, chtpy, with the presence of POMs under mild hydrothermal conditions [8]. Chen's research group has also reported the decarboxylation and transformation of pyridine-2,3-dicarboxylic acid into NA (NA = nicotinic acid) by hydrothermal method [9]. Peng and co-workers' experiments confirmed the in situ hydrothermal synthesis of 5-(4-bromophenyl)picolinic acid (bpa) from 5-(4-bromophenyl)-2-(pyridin-4-yl)pyridine (bppy) with the presence of POMs [10]. They provide a pathway for generating new compounds.

In current work, $H_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 20H_2O$ is used as building blocks and 1,3-bis(4-pyridyl)propane as ligand in order to construct organic–inorganic hybrid materials. Two novel POM-based compounds have been obtained as unpredicted products. It is interesting to note that bpp is transformed into pyridine-4-carboxylic acid (see Scheme 1). This is the first time that oxidation cracking reaction of C—C bonds of an N-heterocyclic ligand occured and pyridine-4-carboxylic acid (PCA) ligand was formed in metal/organic/POM reaction system under hydrothermally conditions.

2. Experimental

2.1. Physical measurements

Distilled water was used in the reactions. $H_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 20H_2O$ was synthesized according to the literature [11] and characterized by IR spectrum in the range 400–4000 cm^{-1} on

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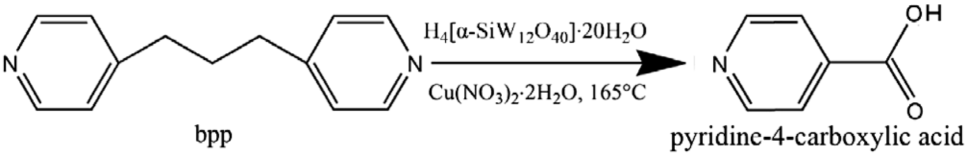

Scheme 1. In situ generation of pyridine-4-carboxylic acid from bpp.

an Alpha Centaurt FT/IR spectrophotometer using KBr Pellets. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Cu and W were determined by a Leaman inductively coupled plasma (ICP) spectrometer. UV spectra were measured using a Shimadzu 3100 spectrometer. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. The magnetic property measurement was performed on crystalline samples with a Quantum Design MPMS-5SQUID magnetometer in the range of 2–300 K.

2.2. Hydrothermal synthesis

Synthesis of $[Cu_2(PCA)_4(H_2O)_2][SiW_{12}O_{40}]\cdot 8H_2O$ (**1**). A mixture of $H_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 20H_2O$ (0.553 g), $Cu(NO_3)_2\cdot 2H_2O$ (0.104 g), bpp (0.03 g) and H_2O (15 mL) was stirred for 20 min in air. The mixture was adjusted to pH 1.9 by the addition 1 mol L^{-1} NaOH aqueous solution. The final solution was then transferred to a 20 mL Teflon-lined autoclave and kept at 165 °C for 4 days. The autoclave was cooled at 10 °C/h to room temperature, the reaction solution was filtered and then the filtrate was kept for 24 h at ambient environment, and blue block crystals of **1** were obtained (35% field based on W). Anal. Calcd for $C_{24}H_{40}Cu_2N_4O_{58}SiW_{12}$ (3673.95): C, 7.85; H, 1.10; N, 1.53; Cu, 3.46; W, 60.05; Si, 0.76(%). Found: C, 7.82; H, 1.17; N, 1.50; Cu, 3.39; W, 60.59; Si, 0.72 (%).

Synthesis of $[Cu(PCA)_2\cdot(H_2O)_4][Cu(PCA)_3\cdot(H_2O)][SiW_{12}O_{40}]\cdot H_2O$ (**2**). The preparation procedure is similar to that for **1**, except that the pH value of the initial reactant was adjusted to 4.5 with 2 mol L^{-1} NaOH. Blue block crystals of **2** were obtained (33% field based on W) after 42 h at ambient environment. Anal. Calcd for $C_{30}H_{37}Cu_2N_5O_{56}SiW_{12}$ (3725): C, 9.67; H, 1.00; N, 1.88; Cu, 3.41; W, 59.23; Si, 0.75 (%). Found: C, 9.65; H, 1.10; N, 1.85; Cu, 3.35; W, 59.20; Si, 0.72 (%).

2.3. X-ray data collection and structure determination

Single crystal data of **1** and **2** were collected on a Bruker Smart Apex CCD diffractometer at 293 K using graphite-monochromate Mo Kα radiation (λ = 0.71069 Å), and omega scans technique, an empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 with *SHELXL-97* software [12]. The non-hydrogen atoms (except O2, O3, O7, O9, O10, O12, O13, O14, Si1, O1W, O2W, O3W, C6 for **1**) were refined anisotropically. Hydrogen atoms were added according to theoretical models. Further details of crystallographic data and structural determination of **1** and **2** are given in Table 1. Selected bond lengths and bond angles of **1** and **2** are listed in Tables S1 and S2.

3. Results and discussion

3.1. Syntheses

Hydrothermal reaction is a useful technique in the preparation of solid state oxides and organic–inorganic materials all the time. In a hydrothermal process, many factors can affect the formation and crystal growth of products, such as the type and stoichiometry of initial reactants, starting concentrations and pH of reaction solution, reaction time and temperature, as well as fill volume [13,14]. By many parallel experiments, we found that when $Cu(NO_3)_2\cdot 2H_2O$ was replaced by $Co(OAc)_2\cdot 4H_2O$ or $NiSO_4\cdot 6H_2O$, we could not obtain the expected compounds. When we adopted a different pH value from that in synthesis of **1**, **2** was separated. On the other hand, an oxidation cracking reaction of C—C bond was observed, that is, bpp was transformed into pyridine-4-carboxylic acid (PCA) in the process of the reactions, different from that reported in Refs. [7,9]. Therefore it is the PCA ligands that coordinate to Cu atoms rather than bpp ligands. The reaction mechanism is not clear but as is well-known, polyoxometalates (POMs) have catalytic-oxidation activity [2], and under presence of POM, the bpp might be oxidized partially by the oxidative materials, such as Cu^{II}, NO_3^-, and O_2 in the acid system under hydrothermal conditions, although Cu^I have not appeared in the product.

3.2. Crystal structure description

The single-crystal X-ray structure analysis reveals that compound **1** is composed of one discrete polyoxoanion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$, dinuclear $[Cu_2(PCA)_4(H_2O)_2]^{4+}$, and eight free water molecules (see Fig. 1). In the Keggin-type polyoxoanion, W—O bonds can be grouped into three sets: W—O_d (terminal) 1.64(3)–1.70(4) Å, W—$O_{b/c}$ (bridge) 1.83(5)–1.93(3) Å, W—O_a (cental) 2.20(9)–2.50(7) Å, consistent with that in Ref. [15]. Due to the orientational disorder of the polyanion the central Si atom is at the center of cube defined by eight oxygen atoms and Si—O bonds range from 1.63(3) to 1.74(2) Å. This kind of disorder often appeared in the $[XM_{12}O_{40}]^{n-}$ Keggin clusters, which was explained by Evans and Pope as a crystallographic result [16].

In **1** there is a crystallographically independent copper atom. The Cu^{II} atom sited on a C_4 axis is coordinated by one water molecule which locates at the axial position [d(Cu—O4W) = 2.16(5) Å], and four oxygen atoms of four PCAs which comprise the equatorial plane [d(Cu—O36) = 1.94(2) Å, d(Cu—O35) = 2.01(2) Å]. The four PCAs acting as bidentate bridging ligands link two Cu^{II} atoms equivalently through their carboxylate groups, forming a dimer cation $[Cu_2(PCA)_4(H_2O)_2]^{4+}$ with paddle wheel shape. In the dimer, Cu(1)—Cu(1#) distance of 2.646(12) Å, indicates a strong Cu—Cu interaction, compared with those reported dimeric structures $[Cu_2^I(DF)_2H_2O][HPMo_{10}^{VI}Mo_2^{V}O_{40}\{Cu^{II}(DF)\}]$ (DF = 4,5-diazafluoren-9-one) (2.543(3) Å) [17a], $[Cu_2(pyBET)_4(H_2O)_2](NO_3)_4\cdot 2H_2O$ (2.669 Å) and $[Cu_2(ppBET)_4(H_2O)_2](ClO_4)_4\cdot 4H_2O$ (2.602 Å) [17b], [Cu(4,4′-bpy)Cl] (2.763(7) Å) [17c], catena-Poly$[Cu_2(OAc)_4(L_1)]\cdot 2H_2O$ (2.642 Å) and catena-Poly$[Cu_2(OAc)_4(L_1)]$ (2.630 Å), catena-Poly$[Cu_2(OAc)_4(L_2)]$ (2.593 Å) and catena-Poly-$[Cu_2(OAc)_4(L_2)]$·solvents (2.614 Å) (L_1 = 1,2-bis(4-pyridyl)ethane, L_2 = 1,4bis(4-pyridyl)buta-1,3-diyne) [17d]. If the second Cu atom is considered as the ligand of the first Cu atom, the Cu atom is in an octahedral surrounding.

Worth mentioning here is that the $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ anions are arranged in an orthorhombic-like body-centered close packing mode, $[Cu_2(PCA)_4(H_2O)]^{4+}$ cations lie at the centers of [001] plane and at between two polyanions in the direction of long cell axis, as shown in Fig. 2A. In the direction of a-axis, adjacent polyanions are linked by water molecules *via* H-bond with O(11)···O1W distance of 2.738 Å, forming a polyanion–water H-bond chain. The four N