Journal of Molecular Structure 1063 (2014) 351–355

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and electrochemical properties of an interdigitated architecture based on Keggin phosphotungstates

Shaobin Li, Huiyuan Ma *, Haijun Pang *, Li Zhang, Zhuanfang Zhang

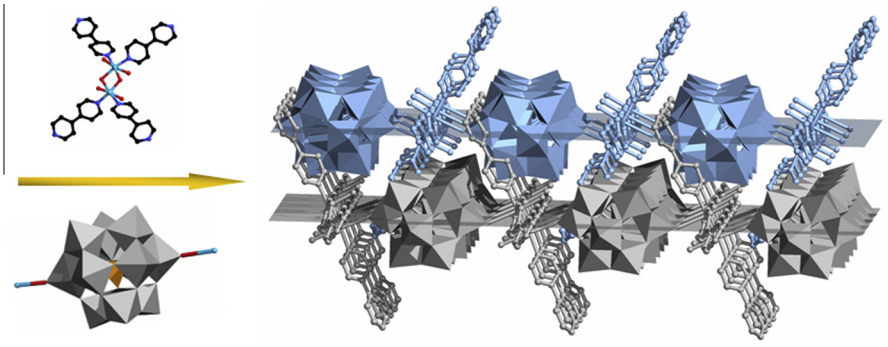
Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, College of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150040, China

HIGHLIGHTS

- A new 3D interdigitated architecture based on Keggin phosphotungstate was obtained.
- The title compound shows a good electrocatalytic activity toward hydrogen peroxide.
- The IR, PXRD, and elemental analyses of the title compound were studied in details.

GRAPHICAL ABSTRACT

A new 2D + 2D → 3D interdigitated architecture was synthesized, which represents the first example of 3D interdigitated architecture based on Keggin phosphotungstates and dinuclear copper(II) complexes.



ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 25 January 2014
Accepted 27 January 2014
Available online 6 February 2014

Keywords:
Polyoxometalates
Dinuclear copper complexes
Interdigitated architecture
Electrochemical properties

ABSTRACT

A new coordination polymer, $[Cu_2(\mu_1\text{-bipy})_2(\mu_2\text{-bipy})(\mu_1\text{-}H_2O)_2(\mu_2\text{-OH})_2(HPW_{12}O_{40})]\cdot 4H_2O$ (**1**) (bipy = 4,4′-bipy), has been synthesized in hydrothermal condition and characterized by elemental analysis, IR spectrum, TG analysis, powder X-ray diffraction and single crystal X-ray diffraction. In **1**, the Keggin PW_{12} clusters as bidentate connectors link dinuclear copper(II) complexes to form a two-dimensional (2D) framework, in which the monocoordinated bipy molecules are orderly appended to both sides of the layer, respectively. Adjacent layers mutually engage in a zipper-like pattern to generate a new 2D + 2D → 3D interdigitated architecture, which represents the first interdigitated architecture assembled by Keggin phosphotungstate clusters and dinuclear copper(II) complexes. Furthermore, the electrochemical properties of **1** were studied, which indicate that **1** has a good electrocatalytic activity toward reduction of hydrogen peroxide.

1. Introduction

Entangled systems represent one fascinating subject in the coordination polymer chemistry. Entanglement compounds such as catenanes, rotaxanes, interdigitation and molecular knots, in which the components are held together by mechanical linkages rather than by covalent bonds, have attracted considerable attention due to not only their abundant architectures and topologies [1–16], but also potential applications ranging from catalysis, drug-delivery vehicles to sensor devices [17–20]. Among the entanglement compounds, interdigitation framework featured by gear-like (or tongue-and-groove) pattern is an intriguing subset,

* Corresponding author. Tel./fax: +86 0451 86392716.
E-mail addresses: mahy017@163.com, mahy017@nenu.edu.cn (H. Ma), panghj116@163.com (H. Pang).

http://dx.doi.org/10.1016/j.molstruc.2014.01.065
0022-2860/

and its unique mechanically interlocked structures are more flexible than the usual networks entirely based on coordination bonds [4].

On the other hand, polyoxometalates (POMs) as early transition metal oxide clusters, are comprised of early-transition metal with d^0 or d^1 electronic configurations (usually $Mo^{VI/V}$, W^{VI}, V^V, Nb^V or Ta^V), which have attracted intense attention during the last two decades not only for their remarkable structural and electronic properties, but also abundant potential applications in catalysis, electrochemistry, medicine, and so on [21–30]. They cover an enormous range in size and structure and thereby provide access to a huge library of readily available and controllable second building units (SBUs). Hence, the introduction of POMs as SBUs brews an appealing route to design novel interdigitated architectures with improved properties [31,32]. However, among the entangled coordination polymers, the POM-based compounds showing entangled structures are very few [33,34], and that showing interdigitated architectures are even rarer. To our knowledge, only four POMs-based interdigitated compounds have been reported: $[Cu_4(bix)_3V_4O_{12}]$ (bix = 1,4-bis(imidazol-1-ylmethyl)benzene) reported by Peng et al. [35], $[Cu_2(bipy)_3(\mu_1\text{-}H_2O)_2(\mu_2\text{-}H_2O)(\mu_2\text{-}OH)(H_2BW_{12}O_{40})]\cdot 4H_2O$ (bipy = 4,4′-bipy), and $[Hdpdo]Ln(Hdpdo)_2(H_2O)_6[H_2W_{12}O_{40}]\cdot nH_2O$ (Ln = Ce and $n = 17$, Ln = Nd and $n = 18$, dpdo = 4, 4′-dipyridine-N,N′-dioxide) reported by our group very recently [36,37].

As a continuation of our previous work, herein, we report a new compound, $[Cu_2(\mu_1\text{-bipy})_2(\mu_2\text{-bipy})(\mu_1\text{-}H_2O)_2(\mu_2\text{-}OH)_2(HPW_{12}O_{40})]\cdot 4H_2O$ (**1**), which represents the first 2D + 2D → 3D interdigitated architecture assembled by Keggin phosphotungstate cluster and dinuclear copper(II) complexes. In addition, the electrochemical studies show that **1** has a good electrocatalytic activity toward reduction of hydrogen peroxide ascribed to W-centers in Keggin PW_{12} cluster.

2. Experimental section

2.1. General procedures

All chemicals were commercially purchased and used without purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer, and that of Cu and W were carried out with a Leaman inductively coupled plasma (ICP) spectrometer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer. A CHI660 electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional three-electrode system was used, with a carbon paste electrode (CPE) as a working electrode, a commercial Ag/AgCl as reference electrode and a twisted platinum wire as counter electrode. The powder X-ray diffraction (PXRD) data were collected on a Rigaku RINT2000 diffractometer at room temperature.

2.2. Synthesis of compound *1*

A mixture of $H_3PW_{12}O_{40}$ (0.346 g, 0.12 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.169 g, 0.69 mmol), 4,4′-bipy (0.0510 g, 0.27 mmol) and 14 mL H_2O was stirred for 1 h at room temperature in air, and pH was adjusted to 4.2 with 1 mol L^{-1} solution of NaOH. Then this mixture was transferred to an 18 mL Teflon-lined reactor, and kept under autogenous pressure at 160 °C for 4 days. After the reactor was slowly cooled to room temperature over a period of 10 °C/h, dark green block crystals of **1** were obtained. The crystals were picked out, washed with distilled water, and dried at room temperature (48% yield based on W). Anal. Calcd for **1**: H, 1.09; C, 9.97; N, 2.32; Cu, 3.51; W 61.01 (%). Found: H, 1.02; C, 9.91; N, 2.41; Cu, 3.63; W, 60.82 (%).

2.3. X-ray crystallography

Single crystal X-ray diffraction data collections of **1** was performed using a Bruker Smart Apex CCD diffractometer with Mo K*a* radiation ($\lambda = 0.71073$ Å) at 296 K. Multi-scan absorption correction was applied. The structure was solved by the directed method and refined by full-matrix least-squares on F^2 using the *SHELXTL* crystallographic software package [38]. We have tried to refine the structure in the $P2_1/n$ group, however, there are many atoms with ADP/NPD problems and the values of R_1/wR_2 are too large ($R_1 = 0.1113$ and $wR_2 = 0.2245$, $[I \geqslant 2\sigma(I)]$). In contrast to $P2_1/n$ group, the structure can be well defined when we refine it in the *Pn* group (please see the detailed information in cif file and Table 1). Positions of the hydrogen atoms on carbon atoms were calculated theoretically. The hydrogen atoms of the water molecules could not be introduced in the refinement but were included in the structure factor calculation. A summary of the crystal data, data collection, and refinement parameters for **1** are listed in Table 1. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 976240.

3. Results and discussion

3.1. Crystal structure

Single-crystal X-ray diffraction analysis reveals that **1** consists of two basic subunits: a dinuclear copper(II) complex $[Cu_2(\mu_1\text{-bipy})_2(\mu_2\text{-bipy})(\mu_1\text{-}H_2O)_2(\mu_2\text{-}OH)_2]^{2+}$ cation (**a**) (Fig. 1a) and a Keggin anion $[HPW_{12}O_{40}]^{2-}$ (PW_{12}) (**b**) (Fig. 1b). In subunit **a**, there are two crystallographically independent Cu atoms (Cu1 and Cu2) (Fig. 1a). Both Cu1 and Cu2 are six-coordinated in an octahedral geometry achieved by two nitrogen atoms of two bipy molecules and one terminal oxygen atom from one PW_{12} cluster and one H_2O molecules and two hydroxyl groups. The bond distances around the Cu atoms are 1.92(2)–2.38(2) Å (Cu—O) and 2.00(2)–2.05(2) Å (Cu—N), and the bond angles are 78.2(8)–199.2(7)° (O—Cu—O) and 96.3(10)–97.3(9)° (N—Cu—N). All of these bond lengths and bond angles are within the normal ranges observed in other Cu(II)-containing complexes [39]. By these

Table 1
Crystal data and structure refinements for compound **1**.

Compound	1
Formula	$C_{30}H_{39}Cu_2N_6O_{48}PW_{12}$
Formula weight	3615.70
Crystal system	Monoclinic
Space group	*Pn*
a (Å)	13.112 (5)
b (Å)	15.777 (5)
c (Å)	14.797 (5)
β (°)	94.721 (5)
V (Å^3)	3050.6 (18)
Z	2
D_{calcd} (g cm^{-3})	3.920
T (K)	293 (2)
μ (mm^{-1})	23.340
Refl. measured	18,315
Refl. unique	8738
R_{int}	0.0462
GoF on F^2	1.071
R_1/wR_2 $[I \geqslant 2\sigma(I)]$	0.0448/0.1080

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.