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Two new organic–inorganic supramolecular hybrids templated by the Wells–Dawson polyoxometalates

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ABSTRACT

Two new supramolecular compounds based on the Wells–Dawson polyoxometalate, $[Cu(Hpbi)_2]_4[P_2W_{18}O_{62}]_2$ (**1**) and $(H_2bbi)_4[Cu_2(bbi)(Hbbi)_2][P_2W_{18}O_{62}]_2$ (**2**) (pbi = 1,1′-(1,3-propanediyl)bis(imidazole), bbi = 1,1′-(1,4-butanediyl)bis(imidazole)), were hydrothermally synthesized and characterized by elemental analyses, IR spectroscopy, thermogravimetric analyses, and single X-ray diffraction. The $[P_2W_{18}O_{62}]^{6-}$ polyanions in both compounds play the template role inducing the metal–organic coordination polymers to array around them. The polymers form 3D supramolecular frameworks with different voids in which the polyanions reside. The difference should be attributed to the different lengths of the two organic ligands. In addition, the electrochemistry properties of the two compounds were studied, which indicates that the supramolecular compounds keep the redox properties of their parent polyanions and exhibit the electrocatalytic activities toward the reduction of bromate and nitrite.

1. Introduction

Polyoxometalates (POMs), one kind of early transition-metal oxide clusters with tunable shapes, controllable sizes and high negative charges, have attracted long-lasting interest in the research areas of magnetism, catalysis, electrochemistry, photochemistry and biological chemistry [1–5]. In virtue of their special properties, POMs are usually employed as excellent inorganic building blocks to combine with the metal–organic frameworks (MOFs) to construct organic–inorganic hybrid materials [6–13]. One of the important areas is the template role of POMs, which means, as large inorganic anions, POMs are suitable as guests for directing the construction of various MOFs with large pores, channels and cavities.

The study on the POM-templated host–guest supramolecules is a rapidly developing domain in hybrid material science. In these supramolecules, the coordination bonds between POMs and the cations are usually very weak, such as weak coordination interactions, electrostatic interactions, and hydrogen bonds [14–20]. Recently, more and more POM-templated host–guest supramolecules are reported and a review by Lu et al. has systematically summarized the former works [21]. In the reported works, we found that such compounds not only exhibit many intriguing architectures but also provide combined peculiarities of POMs and MOFs. On the one hand, due to the various sizes and shapes, the POM templates could control and adjust the void sizes/shapes of MOFs. On the other hand, the MOF supports could conquer the inherent drawbacks of POMs (such as the low specific surface area and the instability in the reaction conditions) to optimize the traditional POM materials. Additionally, the supramolecular compounds have potential applications in gas storage, separation, catalysis and drug delivery [2,22–25]. At present, the POM-templated host–guest supramolecules are mostly focusing on the Keggin POMs, other POMs, such as Lindquist, octamolybdate, decavanadate are also reported [21,26–29]. However, such compounds based on the Wells–Dawson POMs are especially rare, the reported examples $[M_2(bpy)_3(H_2O)_2(ox)][P_2W_{18}O_{62}]_2(H_2bpy)\cdot nH_2O$ (M=Co(II), $n = 3$ (1); M=Ni(II), $n = 2$ (2)) are based on the rigid organic ligands bpy and ox (bpy = 4,4′-bipyridine; ox = $C_2O_4^{2-}$), in which the MOFs form regular host porous to hold the POMs [30]. Herein, we adopt two flexible organic ligands with different lengths (Scheme 1) and construct two Wells–Dawson POM-based compounds, $[Cu(Hpbi)_2]_4[P_2W_{18}O_{62}]_2$ (**1**) and $(H_2bbi)_4[Cu_2(bbi)(Hbbi)_2][P_2W_{18}O_{62}]_2$ (**2**). In both compounds, the Wells–Dawson POMs act as templates directing the MOFs to array around them to construct the host–guest supramolecules.

2. Experimental

2.1. Materials and general procedures

All reagents were purchased commercially and used without further purification. The ligands pbi and bbi were prepared according to the reported procedure [31]. Elemental analyses (C, H, and

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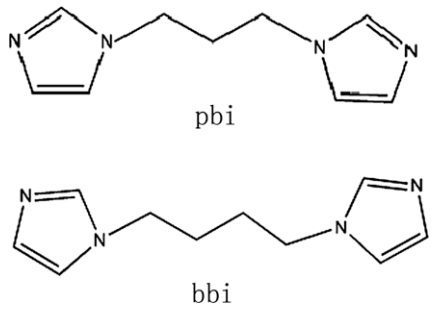

Scheme 1. The ligands used in the construction of the two compounds.

N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Cu was determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. The thermal gravimetric analyses (TGA) were carried out on the Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C/min. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as a counter electrode and Ag/AgCl electrode was referenced. Chemically bulk-modified carbon paste electrodes (CPEs) were used as working electrodes.

2.2. Syntheses

2.2.1. $[Cu(Hpbi)_2]_4[P_2W_{18}O_{62}]_2$ (**1**)

A mixture of α-$K_6[P_2W_{18}O_{62}]\cdot 12H_2O$ (960 mg, 0.2 mmol), $Cu(OAc)_2\cdot H_2O$ (80 mg, 0.4 mmol), pbi (88 mg, 0.5 mmol), triethylamine (trea) (0.1 mmol) and H_2O (10 mL) was stirred for 1 h. The pH was adjusted to about 4.30 with 0.4 mL 1 M HCl, and then the mixture was transferred to an 18 mL Teflon-lined reactor and kept under autogenous pressure at 170 °C for 5 days. The reactor was slowly cooled to room temperature over a period of 10 °C/h. Brown block crystals of **1** were filtered, washed with water, and dried at room temperature. Yield: 41% based on Cu. $Cu_4C_{72}H_{104}N_{32}P_4W_{36}O_{124}$ (10398.0565): Calcd: C, 8.32; H, 1.01; N, 4.31; Cu, 2.44%; Found: C, 8.29; H, 1.03; N, 4.35; Cu, 2.48%. IR (solid KBr pellet, cm^{-1}): 3735 (w), 3437 (s), 2927 (w), 2273 (w), 2165 (w), 1648 (m), 1492 (m), 1447 (w), 1384 (s), 1275 (w), 1228 (w), 1120 (s), 948 (m), 903 (w), 801 (w), 675 (s), 519 (w), 465 (w).

2.2.2. $(H_2bbi)_4[Cu_2(bbi)(Hbbi)_2][P_2W_{18}O_{62}]_2$ (**2**)

The preparation of compound **2** was similar to that of **1** except that the ligand bbi (95 mg, 0.5 mmol) was used instead of pbi. The yield is 42% based on Cu. $C_{70}H_{108}Cu_2N_{28}P_4W_{36}O_{124}$ (10194.9479): Calcd: C, 8.25; H, 1.07; N, 3.85; Cu, 1.25%; Found: C, 8.33; H, 1.03; N, 3.82; Cu, 1.29%. IR (solid KBr pellet, cm^{-1}): 3128 (w), 1630 (w), 1555 (s), 1528 (w), 1438 (w), 1411 (w), 1293 (w), 1219 (w), 1092 (s), 1058 (s), 966 (s), 892 (m), 783 (s), 612 (w), 519 (w).

2.3. X-ray crystallography

Crystal data for compounds **1** and **2** were collected on a Bruker SMART-CCD diffractometer, with Mo Kα monochromatic radiation at 293 K, respectively. The structures were solved by the directed methods and refined by full matrix least-squares on F^2 using the SHELXTL crystallographic software package [32,33]. Crystallographic data are given in Table 1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC numbers 750870 for **1**, 750871 for **2**.

Table 1
Crystal data and structure refinements for compounds **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{72}H_{104}Cu_4N_{32}P_4W_{36}O_{124}$	$C_{70}H_{108}Cu_2N_{28}P_4W_{36}O_{124}$
M_r	10398.0565	10194.9479
Temp. (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71069
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	13.8184(12)	14.762(5)
b (Å)	15.5650(14)	26.185(5)
c (Å)	21.4812(18)	21.228(5)
α (°)	92.4470(10)	
β (°)	90.8860(10)	92.953(5)
γ (°)	111.6080(10)	
V (Å^3)	4289.2(6)	8195(4)
Z	1	4
D_c (mg cm^{-3})	4.023	3.721
μ (Mo Kα) (mm^{-1})	24.655	25.534
Final R_1[a],	0.0600	0.0411
wR_2[b] [$I > 2\sigma(I)$]	0.1475	0.0454
Goodness of fit	0.928	0.834

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

3. Results and discussion

Compounds **1** and **2** were synthesized under almost the same hydrothermal conditions except for using the organic ligands with different lengths. The copper atoms in compounds **1** and **2** are all in +I oxidation state, confirmed by charge balance, coordination environments, bond valence sum (BVS) calculations [34], and crystal color. All W atoms are in the +VI oxidation state. The change of $Cu^{II} \rightarrow Cu^{I}$ may be due to the addition of reductant triethylamine, which is usual under hydrothermal conditions [35,36]. For the charge balance and coordination environments, all the uncoordinated nitrogen atoms in the organic ligands are protonated, which is similar to the reported cases [37,38]. So the compounds could be formulated as $[Cu(Hpbi)_2]_4[P_2W_{18}O_{62}]_2$ (**1**) and $(H_2bbi)_4[Cu_2(bbi)(Hbbi)_2][P_2W_{18}O_{62}]_2$ (**2**).

3.1. Structure description of compound **1**

The single crystal X-ray diffraction analysis shows that compound **1** is built up from one $[P_2W_{18}O_{62}]^{6-}$ (abbreviated as P_2W_{18}) polyanion, two Cu^{I} cations and four pbi ligands (Fig. 1).

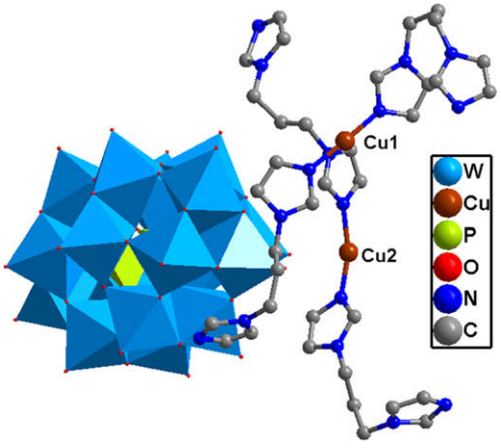

Fig. 1. Stick/polyhedral representation of the asymmetric structure unit of compound **1**. The hydrogen atoms are omitted for clarity.