



Short communication

Synthesis and catalytic activities of two new extended Preyssler-type tungstophosphates with different cavity centers



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ABSTRACT

Two new extended Preyssler-type polyoxometalates (POMs) constructed by Fe(III), 2,2'-biimidazole and Preyssler-type tungstophosphate anions with Na and Ag cavity centers respectively, namely $\{(H_4biim)_5H[Fe(H_2biim)(H_2O)_2(ZP_5W_{30}O_{110})] \cdot 17H_2O\}_n$ ($Z = Na$, compound **1**; $Z = Ag$, compound **2**; $H_2biim = 2,2'$ -biimidazole), were designed and synthesized under hydrothermal conditions, and were systematically characterized by physico-chemical and spectroscopic methods. The two compounds are isostructural coordination polymers. In compound **1** or **2**, there exists interesting infinite 1D chains composed of Preyssler-type $[ZP_5W_{30}O_{110}]^{14-}$ (abbreviated as $\{ZP_5W_{30}\}$) polyanions bridged by Fe(III)-complex fragments, and these chains further formed 3D supramolecular frameworks via extensive hydrogen-bonding interactions. Especially for compound **2**, two types of transition metals, i.e. one Ag^+ ion as a center in the inner cavity and two Fe^{3+} ions as modified cations on the outer surface of one $\{ZP_5W_{30}\}$ unit, existed in the same compound. Additionally, the electrochemical behaviors and acid catalytic activities of compounds **1** and **2** have been investigated.

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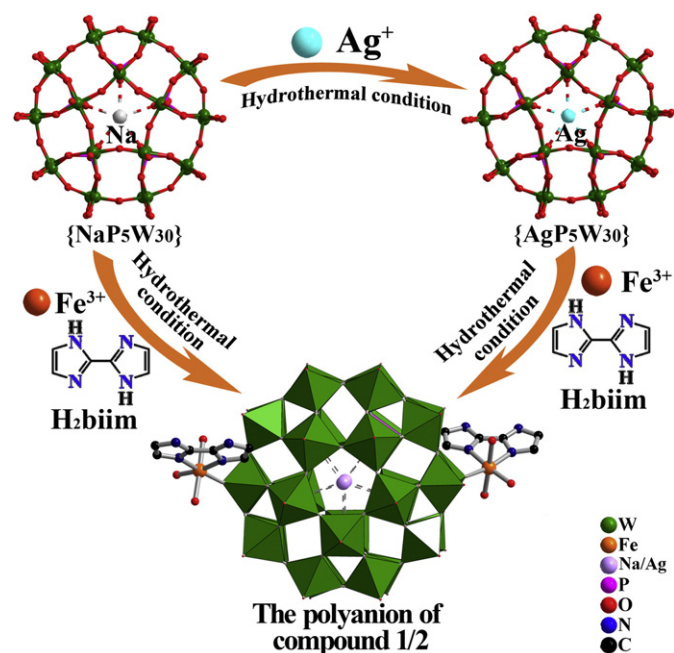
As a kind of well-known metal-oxo-cluster compounds, polyoxometalates (POMs) have aroused wide concern due to their controllable molecular size, inimitable structural features and promising applications in catalysis, electrochemistry and material science [1]. The oxygen-rich surface of POM can be modified by transition metal-organic complexes [2]. The Preyssler-type polyanion cluster $[ZP_5W_{30}O_{110}]^{14-}$ ($\{ZP_5W_{30}\}$) with an inner cavity and 30 terminal O atoms, as one of largest phosphotungstate clusters, possesses unusual doughnut-shaped structure and exhibits remarkable physico-chemical stability [3]. The $\{ZP_5W_{30}\}$ polyanions can capture different cations with appropriate size, such as various alkali, alkaline-earth, transition metal, lanthanide and actinide cations on the inner surface of the polyanion [4], and provide opportunities to bind metal ions or metal-complexes forming extended hybrid materials [5]. That is to say, Preyssler-type polyanion can be modified both on its surface and in its inner cavity. Therefore, $\{ZP_5W_{30}\}$ polyanions can be regarded as promising building blocks to construct novel POM-based inorganic-organic hybrid materials with distinct properties. For example, a series of Preyssler-type polyanion-based inorganic-organic hybrid materials containing different first-row transition-metal ions (e.g., Cu(II), Ni(II), or Co(II) ions) and N-donor polydentate ligands have been reported by Wang's and Sun's groups, respectively [6]. However, in the above Preyssler-type polyanion-based hybrid materials, the introduced transition metal ions located on their exteriors only. In 2014, a 3D Preyssler-type

POM-based coordination polymer decorated with transition metal Ag(I) complex has been harvested. In this work, Ag^+ ions exist both in the inner cavity and the exterior of the Preyssler-type polyanion [7]. Nevertheless, a Preyssler-type polyanion modified by different kinds of transition metal ions both on its surface and in its cavity has not been reported. The main reason is that it is difficult to isolate and purify the $\{ZP_5W_{30}\}$ polyanion encapsulated with metal ions and to find suitable synthesis method to obtain high-quality single crystals. 2,2'-biimidazole (H_2biim), a kind of N donor ligand, possessing effective and multiple coordination ability as well as intricate hydrogen-bond interaction [8], can be introduced into the skeleton of the Preyssler-type polyanion to form high quality inorganic-organic hybrid crystalline materials. Herein, two new extended Preyssler-type polyoxometalates with the same structure and different inner cavities modified by Fe(III) and 2,2'- H_2biim/H_2O , $\{(H_4biim)_5H[Fe(H_2biim)(H_2O)_2(ZP_5W_{30}O_{110})] \cdot 17H_2O\}_n$ ($Z = Na$, compound **1**; $Z = Ag$, compound **2**) were successfully harvested by hydrothermal method from a system inclusion of $\{NaP_5W_{30}\}/\{AgP_5W_{30}\}$ polyanion, $FeCl_3 \cdot 6H_2O$, H_2biim and H_2O (Scheme 1) [9]. The acid catalysis activities of the as-prepared compounds were explored. In addition, the optimal catalytic conditions and reusability of the catalysts were researched in detail.

Single crystal X-ray structural analysis [10] reveals that compounds **1** and **2** are isomorphic compounds, their asymmetric unit contains three types of subunits, i.e. a $\{NaP_5W_{30}\}/\{AgP_5W_{30}\}$ polyanion, one $[Fe(H_2biim)(H_2O)_2]^{3+}$ and five $[H_4biim]^{2+}$ cations (Figs. S1 and S2). The structures of the $\{ZP_5W_{30}\}$ polyanions in the two compounds are essentially the same as the $\{NaP_5W_{30}\}$ derivative previously reported in

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Scheme 1. Designation and synthetic process of compound 1/2.

1985 [11]. Compared with compound **1**, there are two types of transition metals in the structure of compound **2**, one transition metal Ag^+ cation as a center is trapped in the inner cavity of a $\{\text{AgP}_5\text{W}_{30}\}$ unit, and two Fe^{3+} ions combined with $\text{H}_2\text{biim}/\text{H}_2\text{O}$ as a complex fragments are hung on the outer surface of a $\{\text{AgP}_5\text{W}_{30}\}$ polyanion. Crystal data and structural refinement parameters of compounds **1** and **2** were listed in Table S1. As shown in Fig. 1a, the $\{\text{ZP}_5\text{W}_{30}\}$ cluster acts as a bidentate ligand and coordinates with two $[\text{Fe}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2]^{3+}$ subunits through the terminal oxygen atoms of two equivalent WO_6 octahedra. All Fe centers exhibit the same six-coordination environments, coordinating with two oxygen atoms (O1W, O2W) from two coordinated water molecules, two oxygen atoms (O38, O40) from two symmetrical $\{\text{ZP}_5\text{W}_{30}\}$ clusters, and two nitrogen atoms (N1, N2) from a H_2biim molecule (Fig. 1c). The bond lengths of Fe1-N are in the range of 2.097(15)–2.105(15) and 2.106(15)–2.110(15) Å for compounds **1**

and **2**, respectively. And the bond lengths of Fe1-O are 1.918(12)–2.116(13) and 1.894(13)–2.102(15) Å for compounds **1** and **2**, respectively (see Tables S2 and S3). Bond valence sum (BVS) calculations [12] show all W, P, Ag, Fe atoms are in +6, +5, +1 and +3 oxidation states in compounds **1** and **2**, respectively, which are consistent with the results of X-ray photoelectron spectroscopy (XPS) analysis (see below). In addition, no protonated O atom was noted on the polyanions, and H protons were added due to charge-balance considerations. As shown in Fig. 1b, each pair of adjacent $\{\text{ZP}_5\text{W}_{30}\}$ polyanions are bridged by one $[\text{Fe}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2]^{3+}$ subunit, forming into infinite 1D linear chains, and further packed into a 3D supramolecular structure through hydrogen bonding interactions ($\text{N-H}\cdots\text{O}/\text{O/W}$ 2.43(3)–3.27(4) and 2.51(3)–3.26(3) Å for compounds **1** and **2**, see Tables S4 and S5) and electrostatic attractions (Fig. 2). The discrete protonated H_2biim molecules ($[\text{H}_4\text{biim}]^{2+}$ cations) (Fig. 2c) fill in the spaces as compensating cations, and the results indicate that the positive charges of $[\text{H}_4\text{biim}]^{2+}$ cations are important for the formation of the final supramolecular network (Fig. 2a, Figs. S3–S5).

The IR spectra of $\{\text{NaP}_5\text{W}_{30}\}$, $\{\text{AgP}_5\text{W}_{30}\}$, compounds **1** and **2** are presented in Figs. S6 and S7. They all exhibit the characteristic vibrations of the $\{\text{ZP}_5\text{W}_{30}\}$ polyanion: $\nu_{\text{as}}(\text{P-O}_a)$ (1168–1076 cm^{-1}), $\nu_{\text{as}}(\text{W-O}_t)$ (925–918 cm^{-1}), and $\nu_{\text{as}}(\text{W-O}_{b/c})$ vibrations (801–762 cm^{-1}) (O_a : central oxygen; O_t : terminal oxygen; $\text{O}_{b/c}$: bridging oxygen) [6,8]. The wide frequency ranges of 3479–3450 cm^{-1} are associated to $\nu(\text{O-H})$ of water molecules. The weak bonds in the range of 3147–2931 cm^{-1} can be assigned to $\nu(\text{C-H})$ of H_2biim molecules. The absorption in the range of 1604–1596 cm^{-1} can be regarded as the stretching vibrations of the imidazole ring [8]. To investigate the thermal stability, thermogravimetric analysis (TG/DTA) was applied, and the result curves of compounds **1** and **2** were shown in Fig. S8. The first weight loss step at 35 to 200 °C is 3.8% (calcd. 3.5%) for compound **1** and 3.6% (calcd. 3.5%) for compound **2**, which are ascribed to the loss of all lattice water molecules. From 200 to 1000 °C, a main weight loss of 13.3% for compound **1** (11.9% for compound **2**) corresponds to the loss of all organic composites, coordinated water molecules and sublimable phosphorus oxide species originating from partly collapse of the $\{\text{ZP}_5\text{W}_{30}\}$ polyoxoanion skeleton. The two exothermic peaks in DTA curves observed at 460 and 605 °C for compound **1** and 472 and 620 °C for compound **2** respectively are assigned to the combustion of the H_2biim molecules and the sublimation of phosphorus oxide species [13]. In addition, there are apparent weight additions appear at 600 °C in TG curves, which could be due to the decomposition of complex $[\text{Fe}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2]^{3+}$ and the formation of iron oxides [14]. In order to further verify the oxidation states of elements in the compounds, XPS analysis was carried out. As shown in Figs. S9 and S10, the XPS spectra exhibit the characteristic peaks of C 1s, N 1s, O 1s, P 2p, W 4f, Fe 2p and Na 1s for compound **1**, and the characteristic peaks of C 1s, N 1s, O 1s, P 2p, W 4f, Fe 2p and Ag 3d for compound **2**, respectively. These results are consistent with the BVS calculation and elemental analysis, which further confirm that all W, P, Ag and Fe atoms are in +6, +5, +1 and +3 oxidation states, respectively [15]. The above results indicate that the $\{\text{NaP}_5\text{W}_{30}\}/\{\text{AgP}_5\text{W}_{30}\}$ polyanion skeleton in compound **1/2** are thermally stable at lower than 400 °C. The experimental and simulated results in powder X-ray diffraction (PXRD) patterns of compounds **1** and **2** are presented in Fig. S11, the main diffraction peaks positions are accordant, indicating the products are in a pure phase. The different intensities of peaks may be caused by the diverse preferred orientations of the powder samples.

The UV-Vis diffuse reflectance spectra of $\{\text{NaP}_5\text{W}_{30}\}$, $\{\text{AgP}_5\text{W}_{30}\}$, compounds **1** and **2** were performed at 200–800 nm at room temperature (Fig. S12). Comparing with the spectra of parents $\{\text{NaP}_5\text{W}_{30}\}$ and $\{\text{AgP}_5\text{W}_{30}\}$, the strong absorption bands at 265 and 350 nm of compounds **1** and **2** respectively are assigned to the $\text{p}\pi \rightarrow \text{d}\pi$ charge-transfer transitions of the $\text{O}_{b/c} \rightarrow \text{W}$ bonds (LMCT). The wide absorption bands at 560 nm for compound **1** and 570 nm for compound **2** respectively are attributed to the d–d transitions of Fe(III) [5b], indicating

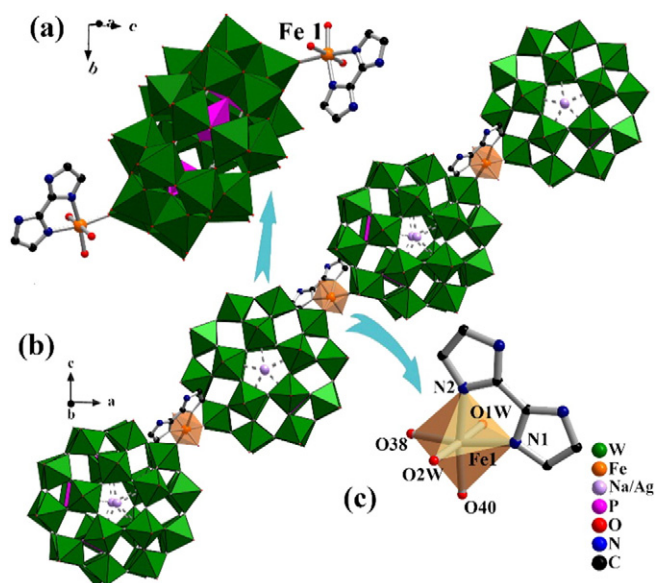


Fig. 1. The polyhedral and ball-and-stick view of the coordination pattern of $\{\text{ZP}_5\text{W}_{30}\}$ (a), the 1D chain (b) and the coordination pattern of Fe(III) (c) in compound 1/2.

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