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A new (2D+1D) polyoxometalate-based *pseudo-rotaxane* framework

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ABSTRACT

A new polyoxometalate-based compound, $[Ag(bbi)][(Ag_2(bbi)_2)(VMo_{12}O_{40})]\cdot 6H_2O$ (**1**) (bbi = 1,1'-(1,4-butanediyl)bis(imidazole), has been synthesized under the hydrothermal condition and characterized by routine methods. Single crystal X-ray diffraction analysis reveals that compound **1** exhibits an interesting (2D+1D) *pseudo-rotaxane* architecture. The electrochemical experiments indicate that **1**-based carbon paste electrode (**1**-CPE) possesses high catalytic efficiency and high stability toward reduction of NO_2^-. Namely, the electrocatalytic efficiency towards the reduction of NO_2^- is *ca.* 364.3% in pH 4.0 CH_3COOH/CH_3COONa containing 16 mM NO_2^-, and the current signal after 100 cycles exhibits almost no loss for **1**-CPE.

1. Introduction

Entangled systems represent one fascinating subject in the coordination polymer. Entanglement compounds such as catenanes, rotaxanes, interdigitation and molecular knots, have attracted considerable attention due to not only their abundant architectures and topologies, but also potential applications [1–8]. *Polyrotaxanes* and *polypseudo-rotaxanes* are a particular species of entangle system, which contain closed two-membered loops and string elements that thread through the loops. Apart from their intrinsic aesthetic appeal, they have potential applications ranging from drug delivery vehicles to sensor devices [9–12].

Polyoxometalates (POMs) are the versatile inorganic building blocks and possess the superior potential applications in catalysis, electrochemistry, biochemistry and biomedical [13–20]. POMs 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 entanglement architectures with improved properties [21]. However, among rapidly increased entangled coordination polymers, the POM-based metal-organic *pseudo-rotaxane* frameworks (MO*P*RFs) are seldom observed. Consequently, the construction of new kinds of POM-based MO*P*RFs is still a difficult task in POM field.

There are several classical POM-based MO*P*RFs have been synthesized by Su, Liao, and Peng et al., which exhibits (3D+1D) [22], (2D+1D) [23] and (1D+0D) [24] *pseudo-rotaxane* frameworks entanglement modes, respectively. Recently, we reported a novel (3D+1D) POM-based MO*P*RFs assembled from Wells-Dawson clusters [25]. As a continuation of our previous work, herein, a new compound, $[Ag(bbi)][(Ag_2(bbi)_2)(VMo_{12}O_{40})]\cdot 6H_2O$ (**1**), has been successfully synthesized. Compound **1** represents the first 2D+1D→3D *pseudo-rotaxane* frameworks assembled by Keggin molybdovanadate clusters and $\{Ag_2\}^{2+}$ dimers.

2. Experimental

2.1. Materials and general methods

All reagents and solvents for syntheses were purchased from commercial sources and used as received without further purification. The elemental analyses were of C, H and N conducted on a Perkin-Elmer 240C elemental analyzer, and that of V and Mo were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. The IR spectra were recorded in the range of 4000–400 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. The X-ray powder diffraction (XRPD) patterns were recorded with a Siemens D5005 diffractometer with Cu-Kα ($\lambda = 1.5418$ Å) radiation. A CHI760D electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional

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three-electrode system was used, with a modified carbon paste electrode (CPE) as working electrode, a twisted platinum wire as counter electrode, and a commercial Ag/AgCl as reference electrode.

2.2. Syntheses of compound 1

A mixture of $Na_3VMo_{12}O_{40}$ (0.2 g, 0.1 mmol), $AgNO_3$ (0.07 g, 0.4 mmol), bbi (0.04 g, 0.2 mmol) and H_2O (15 mL) was stirred for 1 h. Then the solution was sealed in a 23 mL Teflon-lined auto autoclave and heated at 170 °C for 4 days with a starting $pH = 4.2$. After slow cooling to room temperature, red block crystals of **1** were filtered, washed with distilled water and dried at room temperature (43% yield based on Mo). Elemental analysis: $C_{30}H_{54}N_{12}O_{46}VAg_3Mo_{12}$ (**1**) (2844.64). Anal. Calcd for **1**: H, 1.91; C, 12.67; N, 5.91; V, 1.79; Mo, 40.47; Ag, 11.38 (%). Found: H, 1.84; C, 12.74; N, 5.98; V, 1.82; Mo, 40.56; Ag, 11.29 (%).

2.3. X-ray crystallography

Single crystal X-ray diffraction data collections of **1** were performed using a Bruker Smart Apex CCD diffractometer with Mo Kα-radiation ($\lambda = 0.71073$ Å) at room temperature. Multi scan absorption corrections were applied. The structure was solved by Direct Methods and refined by full-matrix least squares on F^2 using the SHELXTL 97 crystallographic software package. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The water molecule could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The SQUEEZE program indicates that there are six solvent water molecules in the crystal structure. Six water molecules were directly included in the final molecular formula based on the elemental analysis and TG analysis. The detailed crystallographic data and structure refinement parameters are summarized in Table 1.

3. Results and discussion

3.1. Structure description of compound 1

The formula of the product was determined to be $[Ag(bbi)][(Ag_2(bbi)_2)(VMo_{12}O_{40})]\cdot 6H_2O$ on the basis of the combined results of X-ray single crystal structure analysis and elemental analysis. Single crystal X-ray diffraction analysis reveals that compound **1** is constructed from three motifs: a Keggin cluster $[VMo_{12}O_{40}]^{3-}$ (abbreviated to VMo_{12}) (**I**), a $\{Ag_2\}^{2+}$ dimer (**II**) and a 1D polymeric chain $[Ag(bbi)]^+$ (**III**) (Fig. 1).

The first motif **I** is a classical α-Keggin type anion. The central V atom is surrounded by a cube of eight oxygen atoms, with each oxygen site half-occupied. The V—O and Mo—O distances are V—O, 1.561(2) to 1.681(3) Å; Mo—O_t, 1.67(2)–1.81(3) Å; Mo—$O_{b/c}$ 1.87(2)–1.94(2) Å and Mo—O_a, 2.39(3)–2.49(3) Å. The valence sum calculations [26] show that all of the Mo atoms are in the +VI oxidation states, the V atom is in the +V oxidation state, and the Ag atoms are in the +I oxidation states.

In the second motif **II**, two 'U'-type bbi ligand are fused by two $\{Ag_2\}^{2+}$ dimers and thus, a tetra-nuclear metal organic circle is obtained. The distances between Ag1 and Ag1 is 3.159 Å, which is shorter than the van der Waals radii of two silver atoms (3.44 Å) [27]. In the circle, the dimension is 13.424×3.159 Å^2 (Fig. S1). Through sharing the same Ag1 ions, the tetra-nuclear circles construct a 1D circle-connecting-circle chain. Furthermore, the Keggin cluster offers two symmetrical terminal O12 atoms to link two Ag1 ions in adjacent circle-connecting-circle chains and a 2D layer (Schläfli symbol: $(4^2\cdot 6^1)$) with quadrangular windows (Fig. 2). The dimension of each window is *ca.* 13.424×14.091 Å (Fig. S2). The VMo_{12} anions in **1** exert their inorganic linkage roles. In the third motif **III**, the 'S'-type bbi ligands use two N donors to coordinate with two Ag2 ions, inducing to a 1D polymeric chain $[Ag(bbi)]^+$. The Ag2 ion is two coordinated by two N atoms from two bbi ligands in line coordination geometry.

The motif **III** and the 2D layer constructed by motifs **I** and **II** are crystallographically distinct subunits. The wave-like chains $[Ag(bbi)]^+$ penetrate the 2D layers at an inclined angle to generate the whole 3D array, as shown in Fig. 4a, exhibiting an interesting *pseudo-rotaxane* architecture. Every 1D chain passes through each quadrangular window (Fig. 3). The structural feature of **1** rests on the *pseudo-rotaxane* topology, which is scarcely observed in POM-based compounds. Furthermore, the wave-like style of 1D chain induces to the stagger-peaked mode of the adjacent 2D sheets. Fig. 4b shows the schematic view of this 3D *pseudo-rotaxane* architecture.

Table 1
Crystal data and structure refinement for **1**.

Formula	$C_{30}H_{54}Ag_3Mo_{12}N_{12}O_{46}V$
Formula weight	2844.64
Crystal system	Triclinic
Space group	$P\bar{1}$
a	12.6599(10)
b	13.2703(10)
c	13.4247(10)
α	66.402(4)
β	70.512(4)
γ	65.786(4)
V/Å^3	1845.8(3)
Z	1
D_{calcd}/g cm^{-3}	2.462
T/K	296(2)
μ/mm^{-1}	2.946
Refl. Measured	24568
Refl. Unique	8473
R_{int}	0.0783
GoF on F^2	1.064
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0964/0.3345

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

3.2. Analyses of IR, TG and XRPD

As shown in Fig. S3, the IR spectrum of **1** exhibits the characteristic peaks at 1069, 961, 869 and 784 cm^{-1}, which are attributed

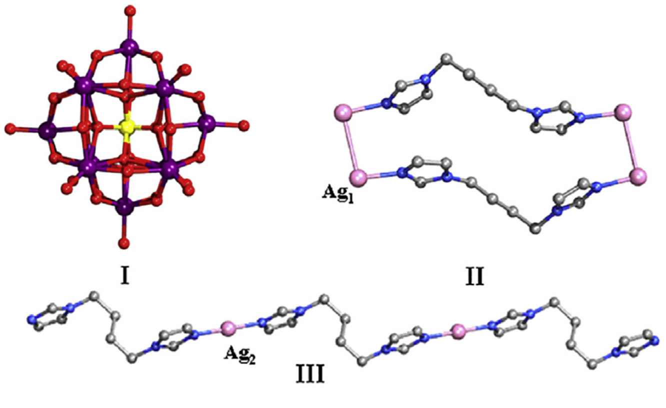

Fig. 1. Three motifs in compound **1**: **I**, the Keggin cluster VMo_{12}; **II**, the tetra-nuclear metal organic circle; **III**, 1D polymeric chain $[Ag(bbi)]^+$.