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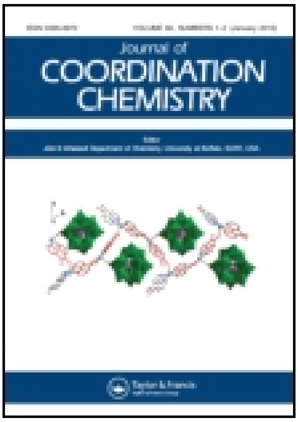

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Assembly of a new Keggin polyoxometalate-templated complex using flexible 1,2-bis(imidazol-1′-yl)ethane ligand

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Assembly of a new Keggin polyoxometalate-templated complex using flexible 1,2-bis(imidazol-1′-yl)ethane ligand

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A new compound, $[\{Cu^{I}(bim)\}_4\{SiW_{12}O_{40}\}]$ (**1**) (bim = 1,2-bis(imidazol-1′-yl)ethane), was hydrothermally synthesized and characterized by elemental analyses, IR, TG, and single-crystal X-ray diffraction. Compound **1** is an infinite 1-D chain composed of Cu-bim coordination polymers and $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ polyanions. The electrochemical and electrocatalytic behaviors of **1**-modified carbon paste electrode (**1**-CPE) have been studied.

Keywords: Keggin-type polyoxometalates; Copper; Flexibility; Electrochemical property

1. Introduction

Polyoxometalates (POMs) have attracted interest due to fascinating nano-sized structures and potential applications in catalysis, medical agents, fluorescent, electronic and magnetic materials [1–9]. With the rapid progress of POMs, particular effort has been devoted to transition-metal coordination polymer (TMCs)-modified POMs, which provides an appealing route to design novel structures with excellent properties [10–14].

Hybrid materials constructed from Keggin, Anderson, Dawson, and Lindquist-type POM clusters and TMCs have been synthesized. Among these, classical Keggin-type polyanions are the most widely developed due to their stability and large number of oxygens as potential sites [15–21]. Our group reported several compounds based on Keggin-type polyanions [22–25]. The choice of proper ligand and transition metal is an effective means to construct a series of TMC-modified hybrids. N-donors with strong coordination capacity have been utilized for building TMCs-modified POM-based inorganic-organic hybrid compounds. It is difficult to obtain structures with high dimensional and interpenetrating topologies by using rigid organic ligands with N-donors, such as pyridyl, pyrazine, and triazole. Compared with rigid ligands, flexible ligands such as 1,2-bis(imidazol-1′-yl)ethane, 1,3-bis(4-pyridyl)propane, and 1,2-bis(1,2,4-triazol-1-yl)ethane show flexibility and conformational freedom, which allow them to conform to the coordination environments of the transition-metal ions and POMs. Cu(I) possesses relatively strong coordination abilities with terminal oxygens of POM and nitrogens of ligand, flexible coordination number from

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*Corresponding authors. Email: hlyukai188@163.com (K. Yu); zhou_bai_bin@163.com (B.B. Zhou) two to seven, and versatile geometries, such as "trigonal bipyramidal," "seesaw," "square pyramidal," T-type, linear [26–28]. These features make it useful as linking units to construct hybrids.

Herein, we choose Cu(I) as metallic linker, flexible 1,2-bis(imidazol-1′-yl)ethane as organic moiety, and Keggin POMs as building blocks to construct Cu-N TMCs-modified POM-based organic–inorganic hybrid compounds. We obtained $[\{Cu^I(bim)\}_4\{SiW_{12}O_{40}\}]$, which shows a 3-D supramolecular structure. Electrochemical and electrocatalytic behaviors of **1**-CPE were investigated.

2. Experimental

2.1. *Materials and general procedures*

All chemicals were obtained from commercial sources and used without purification. $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O$ was prepared according to the literature method [29] and verified by the IR spectrum. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400 CHN Elemental Analyzer. Cu, Si, and W analyses were performed on a PLASMA-SPEC (I) inductively coupled plasma atomic emission spectrometer. IR spectra were obtained on an Alpha Centaurt Fourier transform IR (FT-IR) spectrometer with KBr pellets from 400–4000 cm^{-1}. The thermogravimetric analyses (TGA) were carried out in N_2 on a PerkinElmer DTA 1700 differential thermal analyzer with a rate of 10 °C/min. Electrochemical measurements were performed with a CHI660 electrochemical workstation. A conventional three-electrode system was used. The working electrode was a carbon paste electrode (CPE), a platinum wire as the counter electrode and Ag/AgCl (3 M KCl) electrode was used as a reference electrode.

2.2. *Preparation of $[\{CuI(bim)\}_4\{SiW_{12}O_{40}\}]$ (1)*

Compound **1** was prepared by the hydrothermal method: $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O$ (2 mM), $Cu(CH_3COO)_2\cdot H_2O$ (3 mM), bim (1 mM), and H_2O (30 mL) were stirred for half an hour in air. Then, the mixture was transferred to a Teflon-lined stainless steel autoclave for 6 days at 170 °C. After slow cooling to room temperature, yellow block crystals were filtered and washed with distilled water (yield 68.6% based on Cu). Elemental Anal. Calcd (%): Si, 0.74; W, 58.41; Cu, 6.77; C, 10.16; H, 1.06; N, 5.93. Found (%): Si, 0.76; W, 58.45; Cu, 6.78; C, 10.13; H, 1.04; N, 5.92.

2.3. *X-ray crystallography*

Single-crystal X-ray data of **1** were collected on a Bruker SMART CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 package [30, 31]. All non-hydrogen atoms were refined anisotropically. Hydrogens on carbon and nitrogen were included at calculated positions and refined with

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

Chemical formula	$C_{32}H_{40}Cu_4N_{16}O_{40}SiW_{12}$
Formula weight	3777.17
T/K	293(2)
λ/Å	0.71073
Crystal system	Triclinic
Space group	$P-1$
a/Å	11.4875(10)
b/Å	13.1312(11)
c/Å	14.0252(19)
α/°	102.1620(10)
β/°	106.9560(10)
γ/°	115.8410(10)
V/Å^3	1675.2(3)
Z	1
D_{Calcd}/Mg m^{-3}	3.774
μ/mm^{-1}	21.862
F (000)	1682
Crystal size/mm	0.50 × 0.30 × 0.20 mm
θ range/°	2.72 – 25.02
Reflections collected/unique	11,272/5677 [$R_{(\mathrm{int})} = 0.0394$]
Data/restraints/parameters	5931/121/493
GOF on F^2	1.012
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0749$, $wR_2 = 0.1767$
R indices (all data)[b]	$R_1 = 0.0786$, $wR_2 = 0.1784$

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

a riding model. The crystal data and refinement parameters of **1** are summarized in table 1. Selected bond lengths and angles are listed in table S1.

2.4. *Preparation of 1-modified CPE (1-CPE)*

Compound **1**-modified carbon paste electrode **1**-CPE was prepared as follows: graphite powder (0.3 g) and **1** (0.03 g) were mixed and ground together in an agate mortar and pestle to achieve a uniform mixture, and Nujol (0.2 mL) was then added with stirring. The resulting paste was packed in a glass tube (3 mm diameter) and a copper rod was inserted through one end of the tube to make electrical contact.

3. Results and discussion

3.1. *Crystal structure of 1*

Single-crystal X-ray analysis reveals that **1** is composed of $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ and Cu-bim subunits (see figure 1). The $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ is the well-known Keggin structure, which is based on a central $\{SiO_4\}$ tetrahedron surrounded by twelve $\{WO_6\}$ octahedra. The twelve $\{WO_6\}$ octahedra may be subdivided into four $\{W_3O_{13}\}$ groups, each composed of three edge-sharing $\{WO_6\}$ octahedra. The four $\{W_3O_{13}\}$ groups are linked by sharing corners and link to the $\{SiO_4\}$ tetrahedron by μ_4-O. The W–O bond lengths can be divided into three types: W–O_t (terminal): 1.650(19) – 1.69(2) Å, W–$O_{b/c}$ (bridge): 1.85(2) – 1.96(2) Å,

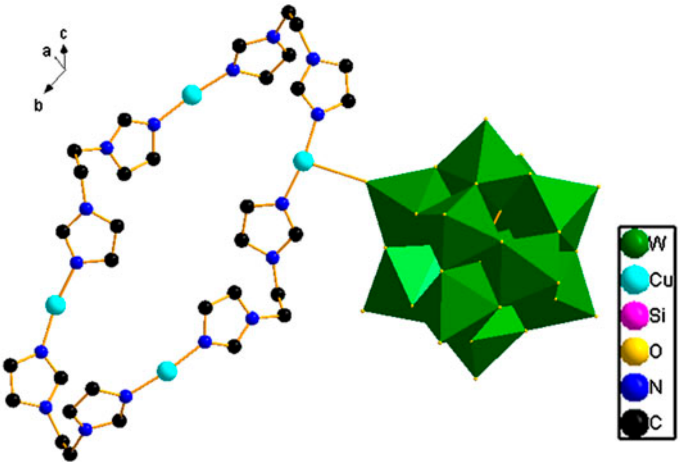

Figure 1. Polyhedral and ball-stick representation of the molecular structure unit of **1**; all hydrogens are omitted for clarity.

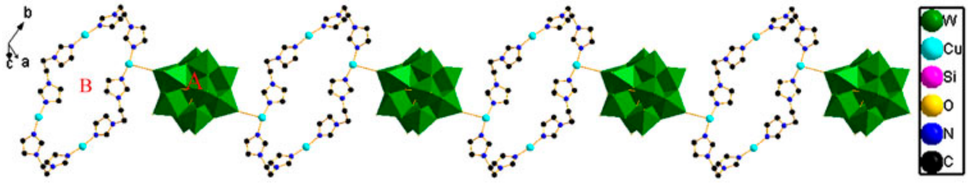

Figure 2. The 1D chain in the "· · ·A–B–A–B–A· · ·" fashion in **1**.

W–O_a (central): 2.33(4) – 2.48(3) Å. The central Si is surrounded by eight oxygens, with each oxygen site half-occupied. The Si–O bond lengths range from 1.55(3) to 1.69(4) Å. This structure often appears in the $[XM_{12}O_{40}]^{n-}$ Keggin clusters, which was explained by Evans and Pope as a crystallographic result [32].

In **1**, there are two crystallographically independent coppers. Cu1 shows linear coordination, coordinating with two nitrogens from two bim (Cu(1)–N(5) 1.87(3) Å, Cu(1)–N(4) 1.88 (4) Å). Cu2 coordinates with one oxygen from $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (Cu(2)–O(1) 2.53(18) Å) and two nitrogens from bim (Cu(2)–N(8)#2 1.87(2) Å, Cu(2)–N(2) 1.90(2) Å) to show a "T-type" mode. The long length and flexibility of bim make it easy to bend to accommodate the coordination environments of copper. In **1**, all bim adopt the "U-type" conformation and exist in a 36-membered ring consisting of four bim ligands and four Cu cations (see figure S1). Each $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ coordinates to two Cu2 (Cu2–O1 2.537 Å) to form a 1-D chain, in which $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ and the rings arrange in the "· · ·A–B–A–B–A· · ·" fashion (see figure 2). Owing to weak C–H· · ·O interactions between $Cu(bim)^+$ and POMs, the 1-D chains are further packed into a 3-D supermolecular framework. Bond valence sum calculations [33] confirm that Si is in the + 4 oxidation state, Cu is in the + 1 oxidation state, and all W are in the + 6 oxidation state. These oxidation states are identical with the charge balance considerations.

3.2. *IR spectrum*

There are four characteristic peaks of POM in **1** (see figure S2): 791 cm^{-1} ascribed to *v*(W–Oc), 881 cm^{-1} ascribed to *v*(W–Ob), 922 cm^{-1} ascribed to the combinations of *v*(W–Od) and *v*(Si–Oa), 964 cm^{-1} ascribed to *v*(W–Od), and 1012 cm^{-1} ascribed to *v*(Si–Oa) [34]. These results indicate that the polyanions in **1** still maintain the basic Keggin structure, only being slightly distorted [35], due to interaction between $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ and Cu complexes. A series of bands from 1112 to 1633 cm^{-1} are associated with the 1,2-bis(imidazol-1′-yl)ethane [36]. This is in agreement with the single-crystal X-ray diffraction analysis.

3.3. *TG analysis*

The thermal analysis of **1** gives a total loss of 33.78% (Calcd 34.07%) from 396 to 516 °C ascribed to decomposition of four 1,2-bis(imidazol-1′-yl)ethane molecules (see figure S3). The TG analysis basically agrees with the structure determination.

3.4. *Voltammetric behavior of 1-CPE*

Owing to insolubility of **1** in water, the CPE becomes an optimal choice to study electrochemical properties. The electrochemical studies of **1**-CPE were carried out in 1 M H_2SO_4 aqueous solution at different scan rates. From −0.8 to 0.75 V, four reversible redox peaks I–I′, II–II′, III–III′, and IV–IV′ are observed with half-wave potentials ($E_{1/2}$) of +0.4521 (I–I′), +0.2013 (II–II′), −0.3982 (III–III′), and −0.5684 (IV–IV′) V (scan rate: 20 mV s^{-1}), where $E_{1/2} = (E_{pc} + E_{pa})/2$; E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively (see figure 3). Redox peaks I–I′ and II–II′ correspond to two consecutive one-electron processes, while III–III′ and IV–IV′ correspond to two consecu-

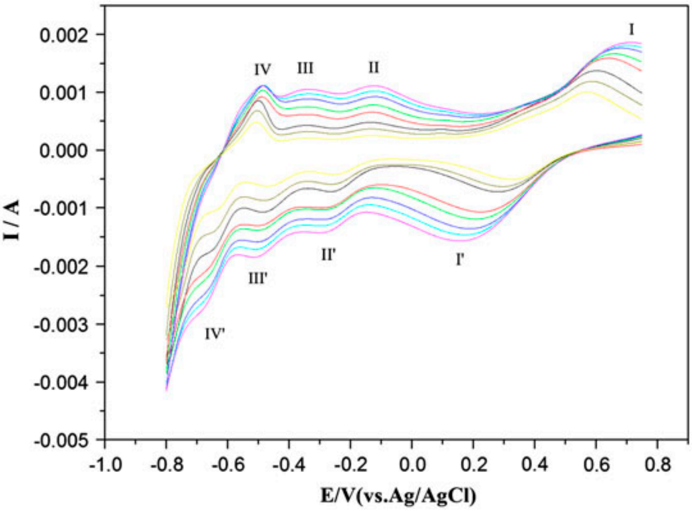

Figure 3. Cyclic voltammograms of **1**-CPE in 1 M H_2SO_4 solution at different scan rates (from inner to outer: 20, 50, 80, 110, 140, 170, 200, 230 mV s^{-1}).

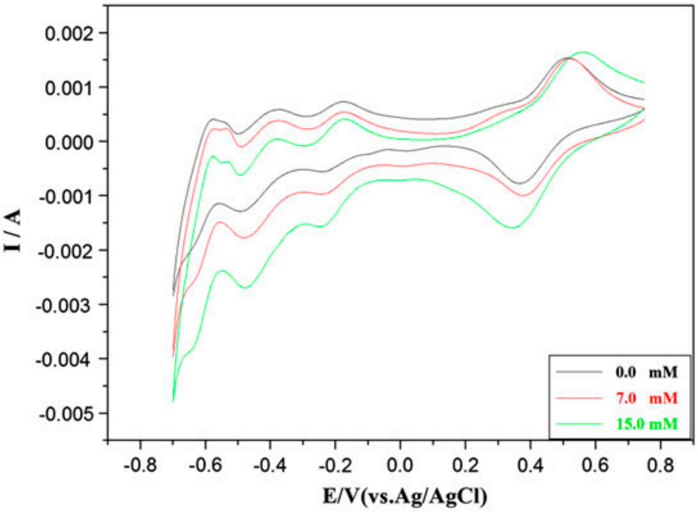

Figure 4. Cyclic voltammograms of **1**-CPE in 1 M H_2SO_4 solution containing 0.0, 7.0, 15.0 mM $NaNO_2$. Scan rate: 20 mV s^{-1}.

tive two-electron processes [37–39]. The cathodic peak potentials shift negative and the corresponding anodic peak potentials shift positive with increasing scan rates. Besides, the peak-to-peak separations between the corresponding anodic and cathodic peaks increased, but the average peak potentials do not change on the whole.

3.5. *Electrocatalytic behavior of 1-CPE*

Keggin POMs can be used as electrocatalysts for reduction in nitrite and hydrogen peroxide in aqueous solutions [40, 41]. figure 4 exhibits cyclic voltammograms for the electrocatalytic reduction in $NaNO_2$ at **1**-CPE in 1 M H_2SO_4 aqueous solution from −0.8 to 0.75 V. With addition of $NaNO_2$, all reduction peak currents increased while the corresponding oxidation peak currents dramatically decreased, suggesting that reduction in $NaNO_2$ is mediated by the reduced species of Keggin-ions in **1**.

4. Conclusions

By using pre-synthesized Keggin-type POM, soft Lewis acidic metal Cu(I) and bim, we obtained a Keggin-type hybrid compound. In **1**, the bim ligands adopt the “U-type” conformation and there exist 36-membered rings consisting of four bim and four Cu cations. Electrochemical analysis shows that **1**-CPE displays unique redox properties and good electrocatalytic activity to reduce nitrite. The synthesis of **1** provides a model for further construction of polyoxometalate-based extended structures.

Supplementary material

CCDC 881997 contains the supplementary crystallographic data for this paper. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

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