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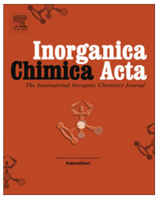

Using imdazole-2-carboxylic and biimdazole-4,4′-dicarboxylic acid to construct Keggin-based mono-nuclear Ag$^+$ subunit and double Cl-capped tri-nuclear Cu$^+$ clusters

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ABSTRACT

Three metal–organic complexes (MOCs) based on Keggin-type polyoxometalate anions and two organic ligands 1*H*-Imdazole-2-carboxylic acid (**L^1**) and 1*H*,1′*H*-Biimdazole-4,4′-dicarboxylic acid (**L^2**), [Ag$_2$(**L^1**)$_4$][HPMo$_{12}$O$_{40}$]·3H$_2$O (**1**), [Ag$_2$(**L^1**)$_4$][HPW$_{12}$O$_{40}$]·H$_2$O (**2**) and [Cu$^{I}_{6}$Cl$_4$(**L^2**)$_6$][H$_3$PMo$_{12}$O$_{40}$]·2NO$_3$ (**3**), have been synthesized under hydrothermal conditions and structurally characterized by single crystal X-ray diffraction analyses, elemental analyses and IR spectra. Complexes **1** and **2** are isostructural and contain a supramolecular chain with a –ABAB– style. The adjacent one dimensional (1D) chains through hydrogen bonding interactions form a 2D supramolecular layer. In complex **3**, there exist double Cl-capped tri-nuclear Cu$^+$ clusters. Furthermore, the photocatalytic and fluorescent properties of complexes **1**–**3** and electrochemical behavior of complexes **2** and **3** were investigated.

1. Introduction

The design and synthesis of inorganic–organic hybrid complexes are extensively attracted in the field of crystal engineering for a long time, not only because of their undisputed hierarchical structural beauty but also their fascinating physical and chemical properties in many fields, such as catalysis, magnetism, gas storage and optical materials [1–4]. From a structural point of view, the selection of apposite inorganic building blocks and organic ligands are the crucial factors for construction of inorganic–organic hybrid complexes. Currently, polyoxometalates (POMs) have been employed as outstanding candidates to construct new inorganic–organic hybrid complexes due to their controllable shapes, high negative charges, abundant coordination modes and various properties [5,6]. Among a variety of different types of POMs, the classic Keggin-type POMs, as an excellent member of POM family, have been extensively recognized and investigated. Up to now, various Keggin-based organic–inorganic hybrid complexes have been synthesized [7–9]. As an ongoing effort, we try to explore the structural features of Keggin-based metal–organic complexes (MOCs) by introducing proper organic subunits.

On the other hand, selection of proper organic ligands may yield novel Keggin-based MOCs with fascinating structures and desirable properties [10,11]. To the best of our knowledge, most of the reported Keggin-based MOCs were constructed by the various N-containing ligands and N/O-containing bis-amides ligands [12,13]. However, Keggin-based MOCs with N-heterocyclic carboxylic acids are still relatively limited reported. In this work, we choose 1*H*-Imdazole-2-carboxylic acid (**L^1**) and 1*H*,1′*H*-Biimdazole-4,4′-dicarboxylic acid (**L^2**) (Scheme 1) as organic ligands for the preparation of different structures with transition metal ions and Keggin anions. We speculate that **L^1** conduces to form mono-nuclear cluster with dispersive N donors. But for **L^2**, we try to explore whether two imidazole rings own short N···N interactions could in favour of chelating metal ions to construct multi-nuclear clusters. It is worth mentioning that the **L^2** ligand is firstly used in the POM field. Furthermore, to the best of our knowledge, the MOCs based on multi-nuclear copper clusters are much less than other transition metal ions, such as Ag$^+$. In view of these points, we chose Keggin-Ag/Cu-**L^1**/**L^2** system in this work to construct novel POM-based MOCs.

In this paper, three new Keggin-based MOCs, [Ag$_2$(**L^1**)$_4$][HPMo$_{12}$O$_{40}$]·3H$_2$O (**1**), [Ag$_2$(**L^1**)$_4$][HPW$_{12}$O$_{40}$]·H$_2$O (**2**) and [Cu$_6$Cl$_4$(**L^2**)$_6$][H$_3$PMo$_{12}$O$_{40}$]·2NO$_3$ (**3**), have been successfully obtained under hydrothermal conditions. Furthermore, the electrochemical behavior of complexes **2** and **3** and the photocatalytic properties of the title complexes have been investigated.

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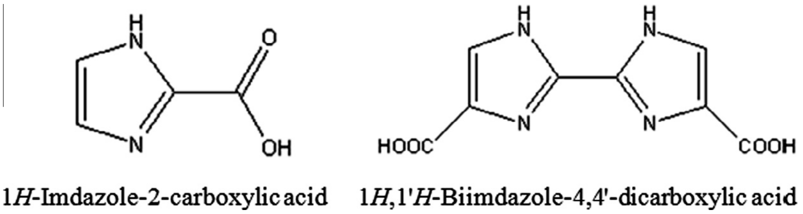

Scheme 1. The ligands 1*H*-Imdazole-2-carboxylic acid (**L**^{1}) and 1*H*,1′*H*-Biimdazole-4,4′-dicarboxylic acid (**L**^{2}) used in this paper.

2. Experience

2.1. Materials and measurement

All the organic solvents and materials used for the synthesis were of reagent grade and used as received without further purification. Elemental analyses (C, H, and N) were carried out on a PerkineElmer 240C elemental analyzer. FT-IR spectra (KBr pellets) were recorded on a on Alpha Centaurt FT/IR spectrometer in the 400–4000 cm^{-1} region. A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for the electrochemical experiments. A conventional three-electrode system was used. The modified carbon paste electrode (CPE) was used as the working electrodes. A saturated calomel electrode (SCE) was used as a reference electrode, and a platinum wire as a counter electrode. UV–Vis absorption spectra were performed on a SP-1901 UV-Vis spectrophotometer.

2.2. Syntheses of title complexes

2.2.1. Synthesis of complex 1

The mixture of $H_3PMo_{12}O_{40}\cdot 26H_2O$ (0.2 g, 0.07 mmol), $AgNO_3$ (0.08 g, 0.47 mmol), and **L**^{1} (0.049 g, 0.2 mmol) was dissolved in 10 mL of distilled water and stirred for 45 mins at room temperature. The pH value was adjusted to 1.80 with 1.0 mol L^{-1} HNO_3 (final pH 1.95). Then, the suspension was sealed into a Teflon-lined stainless steel autoclave (25 mL) and kept under autogenous pressure at 160 °C for 3 days. Slow cooling of the reaction mixture to room temperature, yellow block crystals were filtered and washed with distilled water (42% yield based on Mo). Elemental *Anal.* Calc. for $C_{16}H_{19}Ag_2N_8O_{51}PMo_{12}$ (2537.29): C 7.56, H 0.75, N 4.41. Found: C 7.60, H 0.72, N 4.39%.

2.2.2. Synthesis of complex 2

The synthesis of complex **2** was similarly to **1** except that $H_3PW_{12}O_{40}\cdot 13H_2O$ (0.22 g, 0.07 mmol) was used instead of $H_3PMo_{12}O_{40}\cdot 26H_2O$. The pH value was adjusted to 1.8 with mol L^{-1} HNO_3 (final pH 2.17). Yellow block crystals were filtered and washed with distilled water (35% yield based on W). Elemental *Anal.* Calc. for $C_{16}H_{15}Ag_2N_8O_{49}PW_{12}$ (3556.09): C 5.39, H 0.42, N 3.15. Found: C 5.43, H 0.47, N 3.11%.

2.2.3. Synthesis of complex 3

A mixture of $H_3PMo_{12}O_{40}\cdot 26H_2O$ (0.2 g, 0.07 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) and **L**^{2} (0.073 g, 0.2 mmol) were dissolved in 10 mL of distilled water and stirred for 45 min at room temperature. The pH value was adjusted to 3.5 with 1.0 mol L^{-1} HCl (final pH 3.72). Then the resulting suspension was put to a Teflon-lined stainless steel autoclave (25 mL) and kept at 160 °C for 3 days. Slow cooling of the reaction mixture to room temperature, red block crystals were filtered and washed with distilled water (18% yield based on Mo). Elemental *Anal.* Calc. for $C_{48}H_{41}Cu_6N_{26}O_{70}PMo_{12}$ (3807.38): C 15.13, H 1.08, N 9.56. Found: C 15.19, H 1.06, N 9.52%.

2.3. Preparation of complex 2 and 3 bulk-modified carbon paste electrode (2- and 3-CPE)

Complex **2** modified CPE (**2**-CPE) was fabricated as follows: the 0.1 g graphite powder and 0.01 g complex **2** in an agate mortar for approximately 30 mins to achieve a uniform mixture, and then was added 0.1 mL of Nujol with stirring. The homogenized mixture was packed into a glass tube with a 1.5 mm inner diameter, and the tube surface was wiped with weighing paper [14]. Electrical contact was established with a copper rod through the back of the electrode. In a similar manner, **3**-CPE were manufactured with complex **3**.

2.4. X-ray crystallography

X-ray diffraction analysis data for complexes **1**–**3** were collected with a Bruker Smart Apex CCD diffractometer with Mo-Ka ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods and refined on F^2 by full-matrix least squares methods using the SHELXTL package [15]. All hydrogen atoms attached to water molecules were not located, but were included in the structure factor calculations. The crystallographic data and structural refinement for the three complexes are summarized in Table 1. Selected bond lengths and angles of **1**–**3** are listed in Tables S1–S3.

3. Result and discussion

3.1. Structural description

3.1.1. Structural description of complex 1

Single-crystal X-ray diffraction analysis reveals that complex **1** is composed of two Ag^+ ions, four **L**^{1} ligands, one $[PMo_{12}O_{40}]^{3-}$ (abbreviated to PMo_{12}) anion and three crystal water molecules (Fig. 1). The PMo_{12} anion presents a classical structure of 'α-Keggin' molecule. The central atom P is surrounded by a cube of eight O atoms with each site half-occupied. The P–O and Mo–O lengths are in the normal ranges. The valence sum calculations show that all the Mo atoms are in the +VI oxidation states, all the Ag atoms are in the +I oxidation states.

There is one crystallographically independent Ag1 ion, which exhibits a linear coordination mode. The Ag1 ion is two-coordinate by two N atoms [Ag(1)–N(1) = 2.150(15) Å] from two different **L**^{1}. The bond angles around Ag1 ion are 164.7(8)° for N–Ag–N and 127.1(13)–127.6(12)° for C–N–Ag.

In complex **1**, there exists a mono-nuclear Ag cluster $[Ag(\mathbf{L}^1)_2]^+$, in which two **L**^{1} ligands fuse one Ag1 ion. These mono-nuclear $[Ag(\mathbf{L}^1)_2]^+$ clusters link PMo_{12} anions through hydrogen-bonding interaction (C4···O6 = 3.196 Å) to construct a supramolecular chain with a –ABAB– style. Moreover, the neighbouring 1D chain is further extended into a 2D supramolecular layer through hydrogen-bonding interactions, as shown in Fig. 2.

3.1.2. Structural description of complex 2

Complex **2** is isostructural with **1**. Single-crystal X-ray diffraction analysis reveals that complex **2** consists of two Ag^+ ions, four