

Syntheses, structures and properties of three Keggin-based metal–organic complexes derived from flexible bis-pyridyl-bis-amide and rigid phenanthroline mixed ligands



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ABSTRACT

Three Keggin-type polyoxometalate (POM)-based metal–organic complexes (MOCs) constructed from mixed ligands of phenanthroline (phen) and flexible bis-pyridyl-bis-amide ligands with different spacer length: $[\text{Cu}_2(\text{SiW}_{12}\text{O}_{40})\text{L}^1(\text{phen})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cu}_2(\text{SiW}_{12}\text{O}_{40})\text{L}^2(\text{phen})_2(\text{H}_2\text{O})_4]$ (**2**) and $[\text{Cu}_2(\text{SiW}_{12}\text{O}_{40})\text{L}^3(\text{phen})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**3**) ($\text{L}^1 = \text{N,N}'\text{-bis}(3\text{-pyridinecarboxamide})\text{-1,2-ethane}$, $\text{L}^2 = \text{N,N}'\text{-bis}(3\text{-pyridinecarboxamide})\text{-1,4-butane}$, $\text{L}^3 = \text{N,N}'\text{-bis}(3\text{-pyridinecarboxamide})\text{-1,6-hexane}$), have been synthesized under hydrothermal conditions and structurally characterized by single crystal X-ray diffraction analyses, elemental analyses, thermogravimetric (TG) analyses, IR spectra and powder X-ray diffraction (PXRD) analyses. Complex **1** exhibits a 2D network, in which $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ (SiW_{12}) anions act as tetradentate linkages. Complex **2** is a 0D structure containing a dinuclear complex cation $[\text{Cu}_2\text{L}^2(\text{phen})_2(\text{H}_2\text{O})_4]^{4+}$ and a discrete SiW_{12} anion. Complex **3** shows a 1D chain structure, in which the SiW_{12} anions as bidentate linkages bridge the adjacent complex cations $[\text{Cu}_2\text{L}^3(\text{phen})_2(\text{H}_2\text{O})_4]^{4+}$. The spacer lengths of the bis-pyridyl-bis-amide ligands play important roles in tuning the structures of the title complexes. In addition, the introduction of the secondary ligand phen shows significant effect on the dimensionalities of POM-based bis-pyridyl-bis-amide complexes. The electrochemical behavior and electrocatalytic properties of complex **3**, as well as the photocatalytic activities of the title complexes have been studied.

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1. Introduction

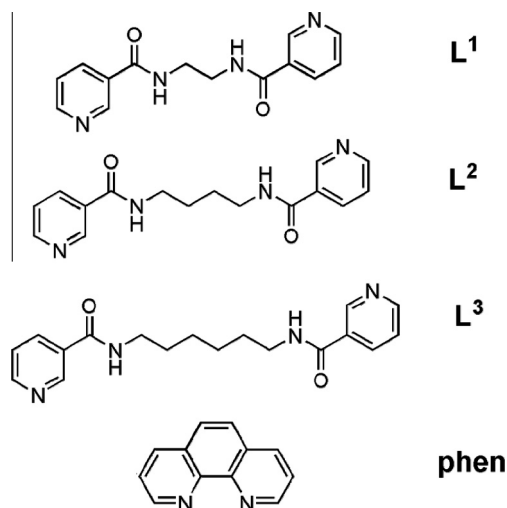
The design and synthesis of polyoxometalates (POMs)-based metal–organic complexes (MOCs) have become an attracting research area in the recent years, not only due to their intriguing variety of architectures, but also for their potential applications in catalysis, molecular adsorption, electron-conductive, optical, biochemical and magnetic materials [1–5]. The proper selection of organic ligands with suitable flexibility and conformational freedom contributes to successful isolation of the POM-based MOCs. The neutral N-donor organic ligands usually lead to the formation of cationic MOC segments, which might satisfy the requirements for POM-based assembly. For example, pyridine- [6], imidazole- [7], trizole- [8], and tetrazole-based [9] ligands have been introduced into the synthesis of the POM-based MOCs. Our group also reported some POM-based MOCs with flexible bis(trizole)- and bis(tetrazole)-based N-donor ligands [10,11]. More recently, the flexible bis-pyridyl-bis-amide ligands have been introduced into

the POM-based MOCs system, due to their flexibility and conformational freedom, as well as their various potential coordination sites and hydrogen bonding interaction sites [12].

It is known that the introduction of mixed N-donor ligands into the POMs system can help to get novel or diverse structures. Wang's group has reported two organic–inorganic hybrids $[\text{Cu}^I(4,4'\text{-bipy})_3][\text{PMo}_{10}^{\text{VI}}\text{Mo}_2^{\text{V}}\text{O}_{40}(\text{Cu}^{\text{II}}(2,2'\text{-bipy}))]$ and $[\text{Cu}^I(2,2'\text{-bipy})\text{-}(4,4'\text{-bipy})_{0.5}]_2[\text{Cu}^I(4,4'\text{-bipy})_2[\text{SiW}_{12}\text{O}_{40}]]$, which are the first examples of POM-based three-dimensional (3D) frameworks constructed with 4,4'-bipyridine(4,4'-bipy) and 2,2'-bipyridine (2,2'-bipy) mixed ligands [13]. Recently, Yan's group also reported several Keggin-based MOCs with mixed ligands [14]. However, to our knowledge, reports on the POM-based MOCs with mixed ligands are still very limited. Based on the consideration above and our previous works, in this work, three flexible bis-pyridyl-bis-amide ligands with different spacer lengths, N,N'-bis(3-pyridinecarboxamide)-1,2-ethane (L^1), N,N'-bis(3-pyridinecarboxamide)-1,4-butane (L^2) and N,N'-bis(3-pyridinecarboxamide)-1,6-hexane (L^3) (Scheme 1), are purposeful selected as the main ligands, and phenanthroline (phen) is used as the secondary ligand to construct Keggin-based MOCs, in order to investigate the effect of the secondary ligand

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Scheme 1. The ligands used in this paper.

and spacer length of the main ligands on the structures of the target MOCs.

In this paper, three new Keggin-based MOCs with three flexible bis-pyridyl-bis-amide and phen mixed ligands have been successfully synthesized under hydrothermal conditions: $[\text{Cu}_2(\text{SiW}_{12}\text{O}_{40})\text{-L}^1(\text{phen})_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cu}_2(\text{SiW}_{12}\text{O}_{40})\text{L}^2(\text{phen})_2(\text{H}_2\text{O})_4]$ (**2**), $[\text{Cu}_2(\text{SiW}_{12}\text{O}_{40})\text{L}^3(\text{phen})_2(\text{H}_2\text{O})_4]\cdot 6\text{H}_2\text{O}$ (**3**). Effects of auxiliary phen ligand and spacer length of bis-pyridyl-bis-amide ligands on the structures of the title complexes have been discussed. The electrochemical behavior of complex **3** and the photocatalytic properties of the title complexes have been investigated. To the best of our knowledge, research on the introducing flexible bis-pyridyl-bis-amide and other N-donor ligands as mixed ligands into POMs systems has not been reported up to now.

2. Experience

2.1. Materials and measurement

All reagents for syntheses were purchased from commercial sources and used as received without further purification. The N-donor ligands L^1 , L^2 and L^3 were prepared according to the reported procedure [15,16]. FT-IR spectra (KBr pellets) were taken on a Varian FT-IR 640 Spectrometer. The elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric (TG) analyses were performed on a Pyris Diamond thermal analyzer under a flowing N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were measured on an Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{ \AA}$) radiation. A CHI 440 electrochemical workstation was used for the electrochemical experiments. A conventional three-electrode cell was used at room temperature. Bulk-modified carbon-paste electrode of complex **3** (**3-CPE**) was used as the working electrode. An SCE and a platinum wire were used as reference and auxiliary electrodes, respectively. UV-Vis absorption spectra were obtained using a SP-1900 UV-Vis spectrophotometer.

2.2. Syntheses of title complexes

2.2.1. Synthesis of complex 1

A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.12 g, 0.5 mmol), L^1 (0.027 g, 0.1 mmol), $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 9\text{H}_2\text{O}$ (0.31 g, 0.13 mmol), phen (0.018 g, 0.09 mmol) and H_2O (10 mL) was stirred for 30 min at room temperature. The pH value was then adjusted to about 4.3 using

1.0 M NaOH. The suspension was transferred to a Teflon lined autoclave (25 mL) and kept at $120\text{ }^\circ\text{C}$ for 6 days. After slow cooling to room temperature with the final pH value of 2.61, blue block crystals of **1** were filtered and washed with distilled water (Yield 40% based on W). Elemental Anal. Calc. for $\text{C}_{38}\text{H}_{38}\text{Cu}_2\text{N}_8\text{O}_{46}\text{SiW}_{12}$: C, 12.31; H, 1.03; N, 3.02. Found: C, 12.34; H, 1.06; N, 3.01%. IR (KBr pellet, cm^{-1}): 3432 (s), 1648 (m), 1642 (w), 1429 (m), 1299 (w), 1116 (m), 975 (m), 919 (s), 796 (s), 719 (m), 619 (m), 536 (m).

2.2.2. Synthesis of complex 2

A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.12 g, 0.5 mmol), L^2 (0.030 g, 0.1 mmol), $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 9\text{H}_2\text{O}$ (0.31 g, 0.13 mmol), phen (0.018 g, 0.09 mmol) and H_2O (10 mL) was stirred for 30 min at room temperature. The pH value was then adjusted to about 4.6 using 1.0 M NaOH. The suspension was transferred to a Teflon lined autoclave (25 mL) and kept at $120\text{ }^\circ\text{C}$ for 6 days. After slow cooling to room temperature with the final pH value of 3.08, green block crystals of **2** were filtered and washed with distilled water. (Yield 36% based on W). Elemental Anal. Calc. for $\text{C}_{40}\text{H}_{42}\text{Cu}_2\text{N}_8\text{O}_{46}\text{SiW}_{12}$: C, 12.86; H, 1.13; N, 3.01. Found: C, 12.82; H, 1.10; N, 3.07%. IR (KBr pellet, cm^{-1}): 3437 (s), 1635 (m), 1578 (m), 1520 (w), 1430 (m), 1315 (w), 1112 (s), 968 (m), 921 (m), 790 (m), 740 (w), 619 (m), 540 (w).

2.2.3. Synthesis of complex 3

A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.12 g, 0.5 mmol), L^3 (0.033 g, 0.1 mmol), $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 9\text{H}_2\text{O}$ (0.31 g, 0.13 mmol), phen (0.018 g, 0.09 mmol) and H_2O (10 mL) was stirred for 30 min at room temperature. The pH value was then adjusted to about 6.0 using 1.0 M NaOH. The suspension was transferred to a Teflon lined autoclave (25 mL) and kept at $120\text{ }^\circ\text{C}$ for 6 days. After slow cooling to room temperature with the final pH value of 2.76, green block crystals of **3** were filtered and washed with distilled water (Yield 34% based on W). Elemental Anal. Calc. for $\text{C}_{42}\text{H}_{50}\text{Cu}_2\text{N}_8\text{O}_{52}\text{SiW}_{12}$: C, 13.06; H, 1.29; N, 2.90. Found: C, 13.03; H, 1.35; N, 2.86%. IR (KBr pellet, cm^{-1}): 3415 (s), 1631 (m), 1502 (w), 1431 (m), 1311 (w), 1112 (s), 970 (m), 922 (s), 796 (s), 721 (w), 619 (m), 530 (w).

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

3-CPE was fabricated by mixing 0.10 g graphite powder and 0.01 g complex **3** in an agate mortar for approximately 30 min to achieve a uniform mixture; then 0.16 mL paraffin oil was added and stirred with a glass rod [17]. The homogenized mixture was packed into a 3 mm inner diameter glass tube and the tube surface was wiped with weighing paper. The electrical contact was established with the copper wire through the back of the electrode.

2.4. X-ray crystallography

Crystallographic data for complexes **1–3** were collected on a Bruker Smart APEX II diffractometer with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$) by ω and θ scan modes at 296 K. All the structures were solved by direct methods and refined on F^2 by full-matrix least squares through the SHELXTL package [18]. All hydrogen atoms attached to water molecules were not located, but were included in the structure factor calculations. The hydrogen atoms on the C atoms were fixed in calculated positions. The hydrogen atoms at N7 and N8 for **1**, N4 for **2** and **3** were located in calculated positions. The disordered O5 for **2**, O10 and O15 for **3** were refined isotropically. All the crystal data and structure refinement details for the three complexes are given in Table 1. The data of relevant bond distances and angles are listed in Tables S1–S3. The hydrogen bond parameters of the title complexes are presented in Tables S4–S6.

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