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Solvent-induced Keggin-based Cd(II)/Ni(II) complexes constructed from pyridyl-tetrazole: Assembly, structures and properties

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ABSTRACT

Three Keggin-based Cd^{II}/Ni^{II} transition metal complexes, namely, $[Cd(3\text{-Hptz})_4(CH_3O)_2](H_3PMo_{12}O_{40})\cdot 2H_2O$ (**1**), $[Cd(4\text{-Hptz})_4(CH_3O)_2](H_3PMo_{12}O_{40})\cdot 2H_2O$ (**2**) and $\{[Ni_3(4\text{-ptz})_2(4\text{-Hptz})_2(\mu_3\text{-O})(H_2O)_2](HPMo_{12}O_{40})\}\cdot 5H_2O$ (**3**) [3-ptzH = 5-(3-pyridyl)-1H-tetrazole, 4-ptzH = 5-(4-pyridyl)-1H-tetrazole], have been synthesized under solvothermal conditions and characterized by IR spectroscopy and single-crystal X-ray diffraction. The mixture of methanol and water was used as the solvent, which play an important role in the formation of compounds **1**–**3**. Compounds **1** and **2** are isostructural. In **1**, four 3-Hptz ligands and two methanol molecules coordinate with one Cd^{II} ion to form a $[Cd(3\text{-Hptz})_4(CH_3O)_2]$ metal–organic unit, which links the adjacent discrete $PMo_{12}O_{40}^{3-}$ (PMo_{12}) anions through hydrogen bonding interactions to construct a 2D supramolecular layer. In compound **3**, the tetrazole groups from one 4-Hptz and two 4-ptz ligands coordinate with three Ni ions to form a flat trinuclear subunit, which is further covered by another 4-Hptz vertically, resulting in a $\{[Ni_3(4\text{-ptz})_2(4\text{-Hptz})_2(\mu_3\text{-O})(H_2O)_2]^{2+}$ cluster. Adjacent trinuclear clusters connect with each other through pyridyl group of 4-ptz ligands to form a 1D chain. The PMo_{12} anions hang on both sides of the 1D chain, and methanol molecules may act as structure-directing agent in **3**. The effect of central metals on the structures of the title compounds was discussed. In addition, the photocatalytic activities of the title complexes for the degradation of methylene blue under UV and sunlight irradiation have been investigated in detail.

1. Introduction

Polyoxometalates (POMs), as a kind of metal oxide clusters, have been widely employed as outstanding inorganic building blocks in the construction of metal–organic complexes (MOCs), because of their oxo-enriched surfaces, highly negative charges, controllable shapes and sizes, as well as their various properties and potential application prospect [1–4]. Up to now, a number of POM-based MOCs have been reported [5–7], most of which were synthesized under hydrothermal conditions [8–10]. Solvothermal technique are relatively scarcely employed in the construction of POM-based MOCs, thus the examples of this kind of complexes obtained under solvothermal conditions are still very limited, to our knowledge. For example, Kong and co-workers obtained a series of Keggin-based hybrid materials with the mixture of acetonitrile and water as solvent [11]. Liu's group obtained several lanthanide-POM frameworks by using ethanol and water as the mixed solvent [12]. Similar to hydrothermal technique, there are also many factors that can influence the assembly and final architectures of POM-based MOCs under solvothermal conditions, such as reactants and their stoichiometry ratios, reaction time, temperature etc. [13–15]. Thus, constructing novel POM-based MOCs with solvothermal technique and exploring the influencing factors would become appealing and challenging.

On the other hand, the choice of central metals seems also important for the construction of POM-based MOCs [16]. In the recent years, most researches focused on the POM-based Cu^{II}/Ag^{I} complexes [17–20]. Reports on the POM-based other transition metals (Zn^{II}, Cd^{II}, Co^{II} and Ni^{II}) complexes are still limited, and most of which were obtained under hydrothermal conditions [21–25]. To the best of our knowledge, only a few POM-based Cd^{II}/Ni^{II} complexes have been synthesized under hydrothermal or solvothermal conditions [26]. Thus, in this work, we selected rigid 5-(*x*-pyridyl)-1H-tetrazole (*x* = 3, 4) ligands to assemble with Cd^{II}/Ni^{II} ions and Keggin-type $PMo_{12}O_{40}^{3-}$ anion under methanol–water mixed solvent conditions, in order to obtain new POM-based Cd^{II}/Ni^{II} MOCs and investigate the effects of organic solvent and central metals on the assembly and structures of target POM-based MOCs. Fortunately, three POM-based Cd^{II}/Ni^{II} complexes have been successfully obtained: $[Cd(3\text{-Hptz})_4(CH_3O)_2](H_3PMo_{12}O_{40})\cdot 2H_2O$ (**1**), $[Cd(4\text{-Hptz})_4(CH_3O)_2](H_3PMo_{12}O_{40})\cdot 2H_2O$ (**2**) and $\{[Ni_3(4\text{-ptz})_2$

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$(4\text{-Hptz})_2(\mu_3\text{-O})(H_2O)_2](HPMo_{12}O_{40})\}\cdot 5H_2O$ [3-ptzH = 5-(3-pyridyl)-1H-tetrazole, 4-ptzH = 5-(4-pyridyl)-1H-tetrazole]. The electrochemical and photocatalytic properties of **1**–**3** have been investigated.

2. Experimental section

2.1. Materials and measurement

All reagents and solvents for syntheses were purchased from commercial sources and used as received. FT-IR spectra (KBr pellets) were recorded on a Varian 640 FT-IR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on an Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with Cu Kα (λ = 1.5406 Å) radiation in the 2θ range of 5–50°. UV–Vis absorption spectra were obtained using a SP-1901 UV–Vis spectrophotometer. Electrochemical experiments were performed with a CHI 440 electrochemical workstation at room temperature. A conventional three-electrode system was used with a saturated calomel electrode (SCE) as reference electrode, the Pt wire as counter electrode, the title compounds bulk-modified carbon paste electrodes (CPEs) as the working electrodes, respectively. Thermogravimetric (TG) analyses were performed on a Pyris Diamond thermal analyzer under a flowing N_2 atmosphere with a heating rate of 10 °C min^{-1}.

2.2. Syntheses of title complexes

2.2.1. Synthesis of complex *1*

$CdCl_2$ (0.03 g 0.13 mmol), 3-ptzH (0.015 g 0.10 mmol) and $H_3PMo_{12}O_{40}$ (0.065 g, 0.035 mmol) were dissolved in the mixed-solvent of 4 mL deionized water and 4 mL methanol (v:v = 1:1). The mixture was put in a 10 ml glass vial and heated at 85 °C for 2 days. After slow cooling to room temperature, yellow block crystals of **1** were obtained and washed with distilled water, and dried in a desiccator at room temperature to give a yield of 43% based on Cd. IR (KBr pellet, cm^{-1}): 3477 (m), 1638 (w), 1573(w), 1059 (m), 958 (s), 877 (m), 796 (s), 743 (m), 675 (m).

2.2.2. Synthesis of complex *2*

Compound **2** was prepared in the same way as **1** except that 4-ptzH was used instead of 3-ptzH. Yellow block crystals of **2** were obtained to give a yield of 45% based on Cd. IR (KBr pellet, cm^{-1}): 3504 (m), 1638 (w), 1544 (w), 1059 (m), 965 (s), 888 (m), 805 (s), 743 (m).

2.2.3. Synthesis of complex *3*

Compound **3** was prepared in the same way as **2** except that $NiCl_2$ was used instead of $CdCl_2$ (0.03 g 0.12 mmol). Blue block crystals of **3** were obtained with a yield of 20% based on Ni. IR (KBr pellet, cm^{-1}): 3425 (m), 1649 (w), 1544 (w), 1450 (w), 1066 (m), 965 (s), 890 (m), 796 (s).

2.3. Preparation of complex *1* bulk-modified carbon paste electrode (*1*-CPE)

The compound **1** bulk-modified carbon paste electrode (**1**-CPE) was fabricated as follows [27]: 0.10 g of graphite powder and 0.010 g of **1** were mixed and ground together by agate mortar and pestle for approximately 30 min to achieve an even, dry mixture; to the mixture 0.15 mL paraffin oil was added and stirred with a glass rod; then the homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.8 cm. The tube surface was wiped with weighing paper and the electrical contact was established with the copper wire through back of the electrode.

2.4. X-ray crystallography

Crystallographic data for compounds **1**–**3** were collected on a Bruker SMART APEX II with Mo Kα (λ = 0.71073 Å) by ω and θ scan mode. All the structures were solved by direct methods and refined on F^2 by full-matrix least squares using the SHELXL package [28]. All hydrogen atoms attached to water molecules were not located, but were included in the structure factor calculations. Moreover, compound **3** exhibits very large solvent accessible voids in the final refinement, the remnant peaks are too weak to be confirmed as solvent molecules. Thus, the SQUEEZE program was used to further estimate the possible voids and the number of solvent water molecules in the crystal structure [29]. The detailed crystal data and structure refinements for **1**–**3** are given in Table 1. Selected bond lengths and angles are listed in Tables S1–S3 (Supporting information). In compound **3**, the five lattice water molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules [30]. The reported refinements are of the guest-free structures using the *.hkp files produced by using the SQUEEZE routine. The amount of water molecules came from the TG experiment.

3. Result and discussion

The solvothermal technique has been regarded as a significant and useful method to construct coordination polymers in recent years. Customarily, solvent plays important roles in the process of constructing the target complexes. It can be employed as ligand, guest or structure-directing agent, which may affect the coordination environments of metal ions and change the connection modes of organic ligands, etc. [31–34]. In our original experiments, we have attempted to synthesize the POM-based Cd^{II}/Ni^{II} complexes under hydrothermal conditions. Unfortunately, we could only get unidentified sediment rather than crystals. However, when we introduced the mixture of CH_3OH/H_2O solvents to replace aqueous solution system, the Cd^{II}/Ni^{II} complexes with different structures were obtained. In this work, when we adjusted the ratios of CH_3OH/H_2O mixed solvents at 1:1 (v:v), two isostructural supramolecular complexes **1** and **2** based on $[Cd(Hptz)_4(CH_3O)_2]$ subunits and PMo_{12} anions can be obtained. The methanol molecules as ligands coordinated with center metal ions in **1**–**2**. However, in **3**, the 1D polymetric chain was constructed by $[Ni_3(4\text{-ptz})_2(4\text{-Hptz})_2(\mu_3\text{-O})(H_2O)_2]^{2+}$ clusters and PMo_{12} anions, no any methanol molecule was included, and it was speculated that methanol might serve as structure-directing agent in **3**. If the ratio of CH_3OH/H_2O mixed solvents is adjusted to 3:1/1:3 (v:v), the yields of the title complexes are far less than those of with 1:1 (v:v) of CH_3OH/H_2O. When methanol was used as single solvent at process of the reaction, we could only get some unidentified sediment. The experimental results indicated that the ratios of CH_3OH/H_2O mixed solvents exhibit obvious influence on the assembly of these POMs-based complexes. Thus, the proper organic solvent and ratio of the mixed solvents seem to be the necessary conditions for synthesis of the title POM-based complexes.

3.1. Structural description of complex *1*

Single-crystal X-ray diffraction analyses reveals that compound **1** consists of one Cd^{II}, four 3-Hptz ligands, one discrete $[PMo_{12}O_{40}]^{3-}$ anion (abbreviated as PMo_{12}), two coordinated methanol molecules and two lattice water molecules (Fig. 1). The central P atom of PMo_{12} is bridged by a cube of eight oxygen atoms with each oxygen atom site half-occupied [35]. The P–O distances range from 1.503(11) to 1.548(7) Å, while the Mo–O bond lengths are in the