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Structures and properties of two coordination polymers constructed by the semirigid bi-functional 5-((1-methyl-1H-tetrazol-5-yl)thio)isophthalic acid ligand

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ABSTRACT

Two new coordination polymers, namely $[Cd(mttia)(H_2O)]_n$ (**1**) and $[Cu(mttia)]_n$ (**2**), have been synthesized with a novel semirigid bi-functional ligand 5-((1-methyl-1H-tetrazol-5-yl)thio)isophthalic acid (H_2mttia) under hydrothermal condition. The two compounds were characterized by single crystal X-ray diffraction, elemental analysis, infrared spectroscopy, thermogravimetric analysis and powder X-ray diffraction. It is demonstrated that compound **1** features a 2D 2-nodal layer with $\{4^3\}_2\{4^6{\cdot}6^6{\cdot}8^3\}$ topology, while compound **2** exhibits a 3D (3,6)-connected framework with $\{4{\cdot}6^2\}_2\{4^2{\cdot}6^{10}{\cdot}8^3\}$ topology. Furthermore, the luminescent property of **1** and the magnetic property of **2** have been studied and discussed.

1. Introduction

As a novel class of crystalline materials, coordination polymers (CPs) have attracted increasing attention due to not only their intriguing network topologies [1] but also their versatile performance in physics and chemistry, such as luminescence [2], magnetism [3], gas adsorption/separation [4], and catalysis [5]. To date, more effort has been devoted to exploring the coordination self-assembly process of metal ions/clusters and various organic ligands to obtain the targeted coordination polymers with desired structures and properties. However, it is still a great challenge to achieve the structure of coordination polymers that could be systematically tailored at the atomic level because many factors may affect the final structure, such as the reaction temperature [6], pH value [7], solvents [8], ratio of reagents [9]. In principle, the reasonable design and synthesis of organic ligands with a favored coordination model is a facile way to modulate new types of coordination polymers with anticipated properties. Therefore, it is of great significance to seek new bridging ligands.

The size, shape and binding sites of organic ligand have been proved to be the most critical factors to the fine-tuning of molecular skeletons and special functionalities. Many rigid ligands, such as multicarboxylic acids [10] and aromatic N-heterocyclic ligands (imidazole [11], triazole [12], tetrazole [13]), have been widely used in the design of coordination polymers with high surface area and porosity owing to their rich coordination modes and high structural stability. Compared to the coordination polymers based on rigid ligands, flexible coordination polymers, which use flexible ligands as building units, have so far provoked unprecedented attention [14]. In contrast to rigid ligands, flexible ligands with free rotation atoms (C, N, O, S) can adjust to various coordination environment by adopting different configurations in the self-assembly process, which no doubt increases the possibility of obtaining the coordination polymers with fascinating topological structures [15]. More importantly, some flexible coordination polymers may have greater potential applications than rigid coordination polymers because of their more significant performance advantages that originate from their flexible nature and dynamic properties, which makes them more attractive in the classes of coordination polymers [16]. Among the flexible coordination polymers, the coordination polymers constructed from flexible polycarboxylic acid ligands [17] or semirigid tetrazole ligands [18] have been widely investigated in recent years. However, there are only a few reports about the flexible bi-functional ligands containing both polycarboxylic acid moieties and tetrazole moieties for the synthesis of coordination polymers [19].

In this work, we have designed and synthesized a new semirigid bi-functional ligand 5-((1-methyl-1H-tetrazol-5-yl)thio)isophthalic acid (H_2mttia) which combines polycarboxylic acid moieties and tetrazole moieties via the mild C–S bonds cross-coupling reaction. The bridging ligand molecule has a flexible thioether functional group between the benzene ring and the substituted tetrazole heterocycle, which affords

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the bridging ligand flexible conformation. Based on this multidentate bridging ligand, two new coordination polymers, namely $[Cd(mttia)(H_2O)]_n$ (**1**) and $[Cu(mttia)]_n$ (**2**), were successfully prepared under hydrothermal condition. Moreover, the single crystal structures, topologies, the luminescent property of **1** and the magnetic property of **2** were also systematically investigated.

2. Experimental section

2.1. Materials and general methods

All the chemical reagents were purchased commercially and used without further purification. Elemental analyses (C, H, N and S) were carried out on a Perkin-Elmer 2400 elemental analyzer. FT-IR spectra were obtained on an Equinox 55 FT-IR spectrophotometer using KBr pellets in 4000–400 cm^{-1} range. ^1H NMR spectra were collected on a Bruker AV-400 spectrometer. Thermogravimetric analyses (TGA) were performed in a nitrogen stream with a heating rate of 10 °C/min using a Pyris1 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) were conducted on an X'Pert PRO automated diffractometer with a 2θ range of 5–50°. Luminescence spectra of crystalline samples were recorded on a FLS920 spectrophotometer. The luminescence lifetime was measured on an Edinburgh FL980 fluorescence spectrometer. Variable temperature (2–300 K) magnetic susceptibility was measured on the Quantum Design SQUID MPMS XL-7 instrument at an applied field of 1000 Oe.

2.2. Synthesis of the ligand

The organic ligand H_2mttia was synthesized via the C–S bond cross-coupling reaction followed by hydrolysis and acidification, as shown in Scheme 1. Dimethyl 5-iodoisophthalate was synthesized according to the procedure in the literature [20].

2.2.1. Dimethyl 5-((1-methyl-1H-tetrazol-5-yl)thio)isophthalate

Dimethyl 5-iodoisophthalate (3.20 g, 10.00 mmol), 1-methyl-1H-tetrazole-5-thiol (1.16 g, 10.00 mmol), CuI (0.01 g, 0.50 mmol), 1,10-phenanthroline (0.18 mg, 1.0 mmol), and K_2CO_3 (1.80 g, 13.00 mmol) were mixed in a 100 mL Schlenk flask. After vacuumized and refilled with N_2 for three times, 50 mL DMF was added. The mixture was stirred at 120 °C for 12 h and then cooled down to room temperature. Ethyl acetate (100 mL) and H_2O (200 mL) were added, and the organic phase was separated. The aqueous phase was then extracted three times with ethyl acetate (50 mL). The obtained organic phase was washed with saturated brine, dried over anhydrous Mg_2SO_4. After removing the organic solvent by rotary evaporation, the residue was purified by column chromatography with petroleum ether/ethyl acetate (3/1, v/v) as eluent. The obtained solution was rotary evaporated to obtain a white solid product (1.85 g, 60.0% yield). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm)=3.960 (s, 6H), 4.047 (s, 3H), 8.392 (d, 2H), 8.707 (t, 1H).

2.2.2. 5-((1-methyl-1H-tetrazol-5-yl)thio)isophthalic acid (H_2mttia)

1.54 g (5.00 mmol) Dimethyl 5-((1-methyl-1H-tetrazol-5-yl)thio) isophthalate was dissolved in THF (50 mL), and then 20 mL 2 M NaOH aqueous solution was added. The solution was stirred at 50 °C for 0.5 h and the THF was removed by rotary evaporation. 6 M HCl was added to the remaining aqueous solution until the solution became acidic (pH = 2–3). The solid was collected by filtration, washed several times with distilled water, and dried under vacuum to give a white solid product (1.29 g, 92.1% yield). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 4.062 (s, 3H), 8.254 (d, 2H), 8.441 (t, 1H), 13.624 (s, 2H).

2.3. Synthesis of $[Cd(mttia)(H_2O)]_n$ (1) and $[Cu(mttia)]_n$ (2)

2.3.1. $[Cd(mttia)(H_2O)]_n$ (1)

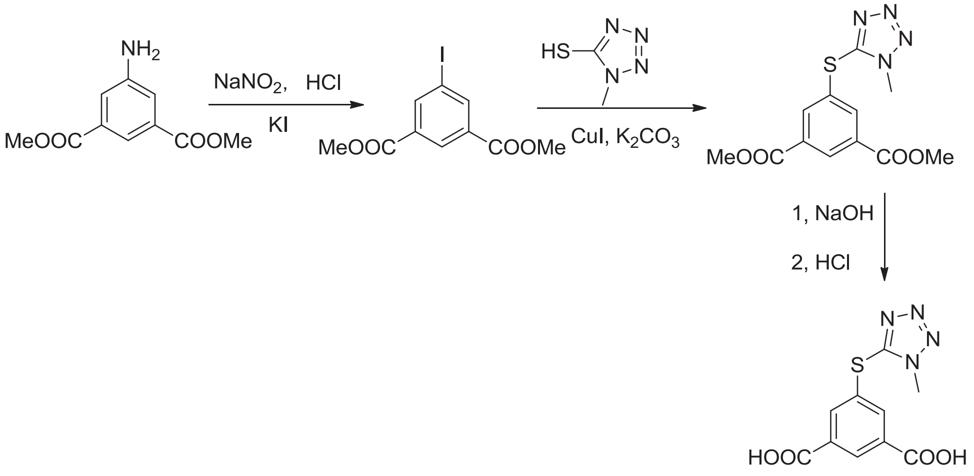
$Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol) and H_2mttia (14.0 mg, 0.05 mmol) were mixed in 4 mL distilled water. 50 μL $NH_3 \cdot H_2O$ (2 M) was added and heated at 120 °C for 48 h, and then cooled down to room temperature at a rate of 5 °C h^{-1}. Colorless crystals of **1** were collected by filtration, washed with distilled water and then dried in the air (yield: 55%, based on the organic ligand). Anal. calcd (%): C, 29.39; H, 1.48; S, 7.85; N, 13.71. Found (%): C, 29.35; H, 1.51; S, 7.87; N, 13.72. IR (KBr, cm^{-1}) (Fig. S1): 3060 (m), 1605 (s), 1560 (s), 1432 (s), 1369 (s), 1287 (m), 1238 (m), 1174 (s), 1170 (m), 922 (m), 778 (s), 727 (s).

2.3.2. $[Cu(mttia)]_n$ (2)

A similar reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (24.2 mg, 0.1 mmol) with H_2mttia (14.0 mg, 0.05 mmol) in 4 mL distilled water containing 50 μL $NH_3 \cdot H_2O$ (2 M) gave green crystals **2** (65% yield, based on the organic ligands). Anal. calcd (%): C, 35.14; H, 1.77; S, 9.38; N, 16.39. Found (%): C, 35.11; H, 1.81; S, 9.42; N, 16.36. IR (KBr, cm^{-1}) (Fig. S1): 3061 (m), 1626 (s), 1575 (m), 1447 (s), 1380 (s), 1271 (m), 1171 (m), 937 (m), 909 (m), 781 (s), 747 (m).

2.4. Single crystal X-ray diffraction

Single-crystal X-ray analysis for compounds **1** and **2** were conducted on a Bruker SMART APEX II CCD based diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. The crystal structures were solved via direct method, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically on F^2 by the full-matrix



Scheme 1. The synthetic route for the ligand.

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