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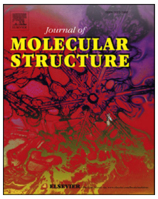

Three interpenetrating coordination polymers with 3D honeycomb networks derived from versatile ligand: 4'-(4-pyridyl)-4,2':6′,4″-terpyridine

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ABSTRACT

Three interpenetrating Co(II)/Ni(II) coordination polymers, $[Co(pytpy)(sfdb)]_n$ (**1**), $[Co_2(pytpy)(sfdb)_2]_n$ (**2**) and $[Ni(pytpy)(sfdb)]_n{\cdot}nH_2O$ (**3**) (pytpy = 4'-(4-pyridyl)-4,2':6′,4″-terpyridine, H_2sfdb = 4,4′-sulfonyldibenzoic acid) have been hydrothermally synthesized and structurally characterized. They all feature interpenetrating 3D honeycomb networks. Compound **1** is a 4-fold 3D polymeric structure, bidentate-bridging pytpy ligands join the square wave-like chains based on Co(II) centers and μ_2-$sfdb^{2-}$ linkers to form the final 3D honeycomb network. Compound **2** is also a 3D honeycomb structure, which features 2-fold interpenetrating structure with unusual paddle-wheel secondary building units (SBUs). The topological net of compound **3** is identical to **1**, but the central metal and its coordination environment are different from those of compound **1**. In addition, diffuse reflectance UV–vis spectroscopic measurements and thermal gravimetry analyses have been used to characterize these compounds.

1. Introduction

Transition metal coordination polymers with well-regulated networks have made considerable progress in the fields of crystal engineering, not only because of their potential applications as new functional materials, but also their intriguing variety of architectures and topologies [1–6]. One of the most common and important structural motif in crystal engineering is honeycomb network, which has the perspective to be used as potential porous materials for separation or catalytic purposes [7–9]. Generally, the honeycomb structures are generated from trigonal nodes (metal center or ligand). As typical trigonal ligands, 1,2,4-Triazolate, 1,3,5-triazine and 2,4,6-tri(4-pyridyl)- triazine, were widely used to construct honeycomb nets with various interpenetrating modes ranging from 2- to 11-fold [10,11]. On the other hand, since typical examples of metal-organic honeycomb networks based on a trigonal metal node and linear organic linkers were reported by Robson, a number of honeycomb networks have been built successfully by using this strategy [12–14].

Herein, a versatile tridentate/bidentate bridging ligand, 4'-(4-pyridyl)-4,2':6′,4″- terpyridine (pytpy, Scheme 1), has been employed to build honeycomb nets. Its rigidity and trigonal geometry may lead to the formation of honeycomb porous frameworks enclosing cavities and channels. Because pytpy is an exotridentate ligand, the nitrogen atoms of three outer pyridyl groups tend to bond with metal ions [15,16]. Our crucial aim of this work is to explore versatile bridging modes of pytpy ligand for tuning the interpenetrating structural assembly, which may provide further insights in designing novel interpenetrating crystalline materials. In this paper, we present the hydrothermal synthesis and crystal structures of three interpenetrating Co(II)/Ni(II) polymeric frameworks, $[Co(pytpy)(sfdb)]_n$ (**1**), $[Co_2(pytpy)(sfdb)_2]_n$ (**2**) and $[Ni(pytpy)(sfdb)]_n{\cdot}nH_2O$ (**3**), as well as their absorption spectra and thermal stabilities.

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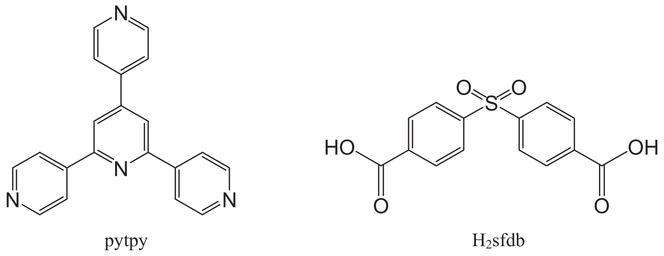

Scheme 1. Molecular structures and abbreviations of the ligands.

2. Experimental section

2.1. General methods

Pytpy was prepared according to literature methods with some modifications [17,18], other chemicals were of reagent grade and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 Fourier transform infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on an elementar Vario EL III elemental analyzer. Fluorescent spectra were recorded on a Hitachi F-4500 spectrophotometer at room temperature. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a rate of 10 °C/min in a nitrogen atmosphere.

2.2. Preparation of $[Co(pytpy)(sfdb)]_n$ (1)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.0238 g, 0.1 mmol), pytpy (0.0312 g, 0.1 mmol), H_2sfdb (0.0306 g 0.2 mmol) in methanol (2.5 mL) and distilled water (10 mL) was placed in a Teflon-lined stainless steel vessel and adjusted the pH value of the mixture to 6.0 with 0.5 mol L^{-1} NaOH aqueous solution. The reaction system was heated at 160 °C for 72 h, followed by slowly cooling down to room temperature at a rate of 5 °C· h^{-1}. Finally, red block crystals were obtained and dried in air, 34.8 mg, yield: 51.7% based on Co. Elemental anal. calcd for $C_{34}H_{22}CoN_4O_6S$ (%): C 60.63, H 3.29, N 8.32; found: C 60.52, H 3.17, N 8.43. IR (KBr, cm^{-1}): 3424 m, 3063 w, 1690 m, 1598 s, 1554 m, 1403 s, 1295 m, 1161 s, 1101 m, 1069 m, 1016 w, 865 m, 826 m, 783 m, 773 w, 741 m, 692 m, 618 m, 572 w, 524 m.

2.3. Preparation of $[Co_2(pytpy)(sfdb)_2]_n$ (2)

Compound **2** was synthesized in a similar procedure as **1**, by adjusting the pH value of the mixture to 4 with 0.5 M NaOH aqueous solution. The rhombus purple crystals of **2** were obtained, 32.7 mg, yield: 63.2% based on Co. Elemental anal. calcd for (%) for $C_{48}H_{30}Co_2N_4O_{12}S_2$: C, 55.61; H, 2.92; N, 5.40. Found: C, 55.73; H, 3.01; N, 5.49. IR (KBr, cm^{-1}): 3432 m, 3073 w, 1691 m, 1647 s, 1610 m, 1512 m, 1405 s, 1301 m, 1161 s, 1101 m, 1015 w, 864 m, 818 m, 737 s, 722 m, 616 m, 571 m, 506 w.

2.4. Preparation of $[Ni(pytpy)(sfdb)]_n \cdot nH_2O$ (3)

This compound was synthesized in a similar procedure as **1**, by using $NiCl_2 \cdot 6H_2O$ (0.1 mmol) in place of $CoCl_2 \cdot 6H_2O$. The rhombus green crystals of **3** were obtained, 46.2 mg, yield: 66.8% based on Ni. Elemental anal. calcd for (%) for $C_{34}H_{24}N_4NiO_7S$: C, 59.07; H, 3.50; N, 8.10. Found: C, 58.96; H, 3.57; N, 8.04. IR (KBr, cm^{-1}): 3492 m, 1609 s, 1563 m, 1534 m, 1402 s, 1289 w, 1161 s, 1101 m, 845 m, 818 w, 782 m, 747 s, 726 m, 621 m, 487 s, 470 m.

2.5. Solid-state UV–vis diffuse reflectance spectra

Solid-state UV–vis diffuse reflectance spectra were performed at room temperature using a Shimadzu UV-2500 double monochromator spectrophotometer. The instrument is equipped with an integrating sphere and controlled by a personal computer. $BaSO_4$ was used as a 100% reflectance standard for all materials. The UV–vis diffuse reflectance measurements of the title compounds were taken in the range 200 nm–700 nm. Data were collected in reflectance (%*R*) mode. Samples were prepared by grinding them to a fine powder and spreading them on a compacted surface of the powdered standard material, preloaded into a sample holder.

2.6. X-ray crystallography

Suitable single crystals of **1**–**3** were selected for X-ray diffraction study. Data collections were performed with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex II CCD diffractometer at 296(2) K. The structures were solved by the direct method and refined by full-matrix least-squares on F^2 with SHELX-97 program package [19]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions. CCDC Nos 763544–763546 (**1**–**3**) contain the crystallographic data for this paper. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk). The crystal data and structural refinement results are summarized in Table 1. The selected bond distances and angles are listed in Table S1.

3. Results and discussion

3.1. Syntheses

Pytpy was synthesized in high purity and acceptable yield according to the method reported by Kröhnke with some modifications, and the reaction time was shorted from 24 h to 7 h. Therefore, our modificative procedure is a more convenient method to preparation of pytpy ligand, as well as its isomeric compounds: 4'-(4-pyridyl)-n_1,2':6′,n_2″-terpyridine ($n_1 = 2, 3, 4$; $n_2 = 2, 3, 4$).

Compounds **1** and **2** were synthesized by the reaction of $CoCl_2 \cdot 6H_2O$ with pytpy and H_2sfdb under similar conditions. When the pH value of the reaction mixture is 6.0, compound **1** was obtained, while change the pH value from 6.0 to 4.0, compound **2** was obtained. Compound **1** is a 4-fold interpenetration 3D honeycomb net with square wave-like chains, while compound **2** is a 2-fold interpenetration 3D honeycomb net with unusual paddle-wheel secondary building units. At higher pH value (6.0), $sfdb^{2-}$ ligands coordinated to Co(II) ions to form square wave-like chain structure, while at lower pH value (4.0), $sfdb^{2-}$ ligands coordinated to Co(II) ions to form paddle-wheel structure. Then pytpy ligands link these square wave-like chain structures or paddle-wheel structures to 3D honeycomb nets. Although pytpy ligand features different bridging modes, they both present interpenetrating 3D honeycomb networks. Compound **3** was prepared in a similar procedure as **1**. The topological net of compound **3** is identical to **1**, but the central metal and its coordination environment are different from those of **1**. Because the angles of coordination nitrogen atoms in pytpy ligands in **1**–**3** are nearly 120°, these compounds have hexagonal honeycomb structures (the angle of coordination nitrogen atoms is 122.32° for **1**, the angles of coordination nitrogen atoms are 122.99°, 118.17° and 119.73° for **2**, and the angle of coordination nitrogen atoms is 122.64° for **3**, see Scheme S1 and Fig. S1). Both of μ_2-and μ_3-pytpy linkers are potential bridging ligands for the