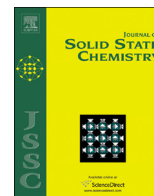




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New 3-D coordination polymers based on semi-rigid V-shape tetracarboxylates

Jing-Jing Huang^{a,b}, Wei Xu^{a,b}, Yan-Ning Wang^{a,b}, Jie-Hui Yu^{a,b,*}, Ping Zhang^{a,*}, Ji-Qing Xu^{a,b}

^a College of Chemistry, Jilin University, Jiefang Road 2519, Changchun 130023, Jilin, China

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Qianjin Road 2699, Changchun 130012, Jilin, China

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ABSTRACT

Under the hydrothermal conditions, the reactions of transition-metal salts, tetracarboxylic acids and *N,N'*-donor ligands yielded three new coordination polymers as $[\text{Cu}_4(\text{fph})_2(\text{bpe})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (fph = 4,4'-(hexafluoroisopropylidene)diphthalate, bpe = 1,2-bis(pyridyl)ethylene) **1**, $[\text{Co}_2(\text{fph})(\text{bpa})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (bpa = 1,2-bis(pyridyl)ethylene) **2**, and $[\text{Ni}(\text{H}_2\text{O})(\text{H}_2\text{oph})(\text{bpa})]$ (oph = 4,4'-oxydiphthalate) **3**. X-ray single-crystal diffraction analysis revealed that the title three compounds all possess the three-dimensional (3-D) network structures. For compound **1**, the fph molecules first link the Cu^{2+} ions into a two-dimensional (2-D) wave-like layer with a (4,4) topology. The bpe molecules act as the second linkers, extending the 2-D layers into a 3-D network. For compound **2**, the fph molecules still serve as the first connectors, linking the Co^{2+} ions into a one-dimensional (1-D) tube-like chain. Then the bpa molecules propagate the chains into a 3-D (4,4,4)-connected network. In the formation of the 3-D network of compound **3**, the oph molecule does not play a role. The bpa molecules as well as the water molecules act as a mixed bridge. Only a kind of 4-connected metal node is observed in compound **3**. The magnetic properties of compounds **1–3** were investigated and all exhibit the predominant antiferromagnetic magnetic behaviors.

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1. Introduction

The rational design and construction of novel metal–organic coordination polymers (CPs) have attracted considerable interests not only because of their aesthetic architectures and topologies [1], but also because of their potential applications as functional materials in the field of ion exchange [2], photoluminescence [3], gas storage and separation [4], heterogeneous catalysis [5], and magnetism [6]. As we know, the formation of metal–organic CPs is influenced by many factors such as organic ligand, solvent, metal ion, pH value, ratio of reactants, and counterion. Among these, the selection of organic ligand is thought to be one of the most important factors, because its shape, length, rigidity/flexibility, and steric effect will directly affect the final frameworks of the as-synthesized metal–organic CPs. Over the last fifteen years, the organic polycarboxylic acid molecules have been verified to be the most remarkable linkers in the construction of novel metal–organic CPs, which may be relevant to the strong ability for the carboxylate groups to form the clusters with the metal ions

[7]. So far, a variety of polycarboxylic acid molecules as the linear dicarboxylic acids [8], the trigonal tricarboxylic acids [9], the tetrahedral or planar tetracarboxylic acids [10], the hexacarboxylic acids [11], and the octacarboxylic acids [12], have been employed, constructing a series of novel metal–polycarboxylate CPs.

Recently, a certain attention has been paid to a class of semi-rigid V-shape tetracarboxylic acid molecules. They consist of two phthalic acid moieties, connected by a non-metallic atom as C ($-\text{C}(=\text{O})-$, $-\text{C}(\text{CF}_3)_2-$), O ($-\text{O}-$) or S ($-\text{S}-$, $-\text{SO}_2-$) atom [13–17]. The so-called V shape derives from the tetrahedral configuration of the centric non-metallic atom, and approximately vertical arrangement of two benzene ring planes. While the so-called semi rigidity means that the tetrahedron for the centric atom can be slightly distorted, and two benzene rings can appropriately rotate around the centric atom. Such semi-rigid V-shape tetracarboxylates-based CP materials, we think, may have the following characteristics: (i) diverse and stable structures. Due to the existence of four carboxylate groups, this kind of tetracarboxylate molecule possesses a potential to exhibit the various coordination modes, linking the metal centers to form the different chains, layers or 3-D networks. Once more O atoms are involved in the coordination, the compounds should have a better stability; (ii) forming a helical or tube-like chain. This should be due

* Corresponding authors. Tel.: +86 431 88499132; fax: +86 431 85168624.

E-mail addresses: jhyu@jlu.edu.cn (J.-H. Yu), zhangping@jlu.edu.cn (P. Zhang).

to its V-shape and semi-rigid structural features. In some reported compounds as $[\text{Ba}(\text{sdpth})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ (sdpth=4,4'-sulfoyl-diphthalhydrazide), the helical or tube-like chains have been observed [14b,15e,17d,18]; (iii) acting as di- or tricarboxylic acid. By controlling the pH value of reactive system, the degree of deprotonation for the tetracarboxylic acid molecules can be regulated. The non-deprotonated carboxyl group can be viewed as a substituent; (iv) nice magnetic property. A variety of strong or weak metal...metal interactions can be observed in the packing structures of the compounds, which provide many potential magnetic exchange paths. In addition, the N,N' -donor ligands are used to modify the metal-polycarboxylate networks. These organic bases play an important role in the extension and stabilization of the metal-tetracarboxylate networks [19]. Up to now, the semi-rigid V-shape tetracarboxylate-based Zn(II) and Cd(II) compounds have been studied extensively. They show the excellent photoluminescence properties. However, the semi-rigid V-shape tetracarboxylate-based Cu(II), Co(II) and Ni(II) compounds were seldom investigated. In this article, two semi-rigid V-shape tetracarboxylic acid molecules, $\text{H}_4(\text{fph})$ and $\text{H}_4(\text{oph})$ (fph=4,4'-(hexafluoroisopropylidene)diphthalate; oph=4,4'-oxydiphthalate) were selected. The reactions of Cu(II)/Co(II)/Ni(II) salts, $\text{H}_4(\text{fph})/\text{H}_4(\text{oph})$ and N,N' -donor ligands were performed, producing three new 3-D metal-organic CPs as $[\text{Cu}_4(\text{fph})_2(\text{bpe})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (bpe=1,2-bis(pyridyl)ethylene) **1**, $[\text{Co}_2(\text{fph})(\text{bpa})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (bpa=1,2-bis(pyridyl)ethylene) **2**, and $[\text{Ni}(\text{H}_2\text{O})(\text{H}_2\text{oph})(\text{bpa})] \cdot 3\text{H}_2\text{O}$ **3**. Herein, we will report their syntheses, crystal structures, thermogravimetric (TG) behaviors and magnetic properties (Scheme 1).

2. Experimental

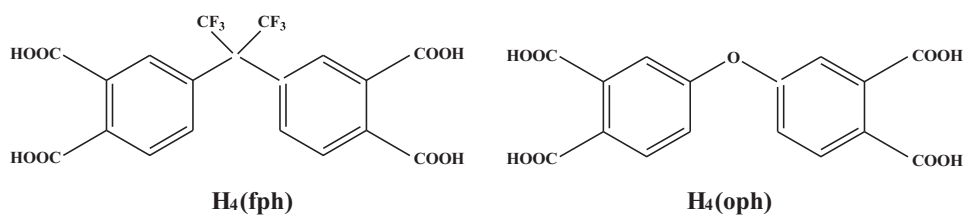
2.1. Materials and physical measurement

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in 4000–400 cm^{-1} region using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). TG behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 $^\circ\text{C min}^{-1}$ in air.

2.2. Synthesis of 1–3

2.2.1. Synthesis of 1

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.2 mmol, 48 mg), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (fpha) (0.1 mmol, 44 mg), bpe (0.1 mmol, 18 mg), and water (10 mL) was adjusted to pH=7 by triethylamine (ca. 0.05 mL), and then heated to 120 $^\circ\text{C}$ in a Teflon-lined stainless steel vessel under autogenous pressure for 3 days, and subsequently cooled to room temperature. The obtained dark-olive block crystals were collected, washed with water, and dried in air. Yield: ca. 25% based on Cu(II). Anal. Calcd for $\text{C}_{74}\text{H}_{50}\text{N}_6\text{O}_{20}\text{F}_{12}\text{Cu}_4$ **1**: C, 48.69; H, 2.76; N, 4.60. Found: C, 48.66; H, 2.76; N, 4.68%.



Scheme 1. Structures of tetracarboxylic acid molecules in 1–3.

IR (cm^{-1}): 1609(s), 1572(m), 1535(m), 1507(w), 1424(s), 1399(s), 1214(w), 1183(m), 967(w), 834(w), 720(w), 554(w).

2.2.2. Synthesis of 2

A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.2 mmol, 50 mg), fpha (0.1 mmol, 44 mg), bpa (0.1 mmol, 18 mg) and water (10 mL) was adjusted to pH=7 by NaOH, and then heated to 120 $^\circ\text{C}$ in a Teflon-lined stainless steel vessel under autogenous pressure for 3 days, and subsequently cooled to room temperature. The obtained purple needle crystals were collected, washed with water, and dried in air. Yield: ca. 30% based on Co(II). Anal. Calcd for $\text{C}_{43}\text{H}_{40}\text{N}_4\text{O}_{13}\text{F}_6\text{Co}_2$ **2**: C, 49.06; H, 3.83; N, 5.32. Found: C, 48.94; H, 3.88; N, 5.26%. IR (cm^{-1}): 3431(s), 1614(s), 1571(s), 1500(w), 1405(s), 1256(s), 1214(m), 1183(m), 1088(w), 1031(w), 986(w), 961(w), 821(m), 713(w), 617(w), 529(w).

2.2.3. Synthesis of 3

A mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol, 44 mg), 4,4'-oxydiphthalic anhydride (opha) (0.1 mmol, 31 mg), bpa (0.1 mmol, 18 mg) and water (8 mL) was adjusted to pH=6 by NaOH, and then heated to 120 $^\circ\text{C}$ in a Teflon-lined stainless steel vessel under autogenous pressure for 3 days, and subsequently cooled to room temperature. The obtained green block crystals were collected, washed with water, and dried in air. Yield: ca. 20% based on Ni(II). Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_{10}\text{Ni}$ **3**: C, 55.57; H, 3.66; N, 4.63. Found: C, 55.27; H, 3.56; N, 4.66%. IR (cm^{-1}): 1678(s), 1620(m), 1577(s), 1431(w), 1386(s), 1260(m), 1228(s), 1126(m), 1069(w), 834(m), 802(m), 688(w).

2.3. X-ray crystallography

The data were collected with $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) on a Siemens SMART CCD diffractometer for compounds **1** and **3**, and on a Rigaku R-Axis RAPID IP diffractometer for compound **2**. With SHELXTL program, all of the structures were solved using direct methods [20]. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement, and the other hydrogen atoms were treated using a riding model. The H atoms on the water molecules in compounds **1–3** were not located. The H atoms on C16, C17 in compound **2**, C14, O3 in compound **3** were not located, either. The structures were then refined on F^2 using SHELXL-97 [20]. CCDC numbers are 1031507–1031509 for compounds **1–3**, respectively. The crystallographic data for the title compounds are summarized in Table 1.

3. Results and discussion

3.1. Synthetic analysis

All of the title compounds were obtained under the hydrothermal conditions. At the different pH levels, the reactions of Cu(II)/Co(II)/Ni(II) salts, $\text{H}_4(\text{fph})/\text{H}_4(\text{oph})$ and N,N' -donor ligands created the title three CPs **1–3**. Based on the synthetic procedures of compounds **1–3**, and some parallel reactions, we can know that (i) the pH value has an effect on the reaction. First of all, the crystal growth of compounds **1–3** is strictly controlled by the pH value of

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