



Research paper

Five metal-organic frameworks based on 5-(pyridine-3-yl)pyrazole-3-carboxylic acid ligand: Syntheses, structures and properties



Jiajia Cheng^a, Shimin Wang^b, Zhan Shi^a, Huan Sun^a, Baojun Li^a, Miaomiao Wang^a, Muyang Li^c, Jinpeng Li^{a,*}, Zhongyi Liu^{a,*}

^a College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan, PR China

^b College of Material and Chemistry Engineering, Henan Institute of Engineering, Zhengzhou 451191, PR China

^c Zhengzhou University, Zhengzhou 450001, Henan, PR China

ARTICLE INFO

Article history:

Received 30 April 2016

Received in revised form 25 July 2016

Accepted 1 August 2016

Available online 2 August 2016

Keywords:

Polymer

Crystal structure

Fluorescence properties

Magnetic properties

ABSTRACT

Five new polymers based on 5-(pyridine-3-yl)pyrazole-3-carboxylic acid (H_2ppca), namely, $[Cd_2(ppca)(bix)(SO_4)]_n$ (**1**), $[Cd(Hppca)_2 \cdot H_2O]_n$ (**2**), $[Mn(Hppca)_2 \cdot H_2O]_n$ (**3**), $[Zn_2(ppca)_2]_n$ (**4**) and $[Cu(ppca)]_n$ (**5**) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction, elemental analyses and IR spectroscopy. Structural analyses reveal that polymer **1** possesses a 2-fold interpenetrating three-dimensional (3D) framework. Polymers **2** and **3** display 4-connected 2D frameworks, while polymer **4** features a (3,3)-connected topology with the Schläfli symbol (4-8-10). **5** exhibits a 2D structure with the Schläfli symbol (4-8²). Furthermore, the fluorescence properties of the five polymers are also investigated in the solid state, showing the fluorescence signal changes in comparing with that of free ligand mbbz. Polymer **5** with square pyramid geometry (τ_{Cu1} , 0.069) implies that there is strong antiferromagnetic interactions between two adjacent Cu1C and Cu1, and the magnetic interactions are mainly transferred by the bridging *N,N*-triazole ligands.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the rational design and preparation of metal-organic frameworks (MOFs) have attracted a great deal of interest not only because of their fascinating structures, but also due to their characteristic physical and/or chemical properties in magnetism, gas storage, catalysis and luminescence [1–5]. Usually, to obtain the metal-organic frameworks with specific structural topologies and properties, many complicated influential factors need to be considered, such as different metal salts, organic ligands, reaction temperature and so on [6–8], among which pre-selected organic ligands are of usually great importance in the construction of coordination architectures [9–11], since it can adjust the coordination mode, flexibility of the molecular backbone, configurational preference, type, and topology of the products by coordinating directly to the metal centers [12]. While in pre-selected organic ligands, organic carboxylate ligands were well employed to construct complexes with fascinating topologies and useful properties [13], because organic carboxylate ligands possess

special metal-coordinating ability and versatile coordination modes, which are possible to make the large diversity of topologies [14]. Moreover, they can be regarded not only as hydrogen bonding donors but also as accepters in the assembly of MOFs structures [15–18]. On the other hand, it is well-acknowledged that the organic ligands containing pyridyl functional group which possess stronger metal-coordinating ability have also been intensely investigated since the variable location of the nitrogen atoms may provide various coordination sites [19,20]. Until now, a number of MOFs with novel topologies and useful properties which contains organic carboxylate or pyridyl functional group ligands have been widely reported [21–23]. The combination of pyridyl functional group, carboxylate group and other N-donors aromatic group in one organic ligand may give rise to intriguing structural motifs and properties.

Based on the above idea, we pre-selected 5-(pyridine-3-yl)pyrazole-3-carboxylic acid (H_2ppca) as ligand. We obtained five new polymers under different hydrothermal conditions, which display multiple topological structures. Herein, we report the synthesis, crystal structures, and fluorescence properties of five polymers based on H_2ppca ligand. The magnetic properties of polymer **5** are also investigated.

* Corresponding authors.

E-mail addresses: ljp-zd@zzu.edu.cn (J. Li), liuzhongyi@zzu.edu.cn (Z. Liu).

2. Experimental section

2.1. Material and measurement

All chemicals were of analytical grade quality and purchased from commercial sources and used without further purification. IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer with KBr pellets in the range of 400–4000 cm^{-1} region. Elemental analyses (C, H and N) were carried out on a Carlo-Reba 1106 elemental analyzer. Fluorescence spectra were characterized at room temperature by a F-4500 fluorescence spectrophotometer (Japan). The excitation slit, as well as the emission slit was 5 nm. Magnetic properties of polycrystalline samples of **5** were measured on a Quantum Design MPMS SQUID magnetometer. The temperature dependence of the magnetic susceptibility was recorded in an applied field of 1000 G in a temperature range 2–300 K. The magnetic responses were corrected with diamagnetic blank data of the sample holder measured separately. The diamagnetic contribution of the sample itself was estimated from Pascal's constants.

2.2. Preparation of the polymers

2.2.1. Synthesis of $[\text{Cd}_2(\text{ppca})(\text{bix})(\text{SO}_4)]_n$ (**1**)

A mixture of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (147.6 mg, 0.10 mmol), H_2ppca (18.9 mg 0.10 mmol), 1,4-[bis(imidazol-1-ylmethyl)benzene] (bix, 2.0 mg, 0.05 mmol), NaOH (8.0 mg, 0.2 mmol) and H_2O (8 mL) was placed in a 10 mL Teflon-lined stainless steel vessel. The mixture was heated at 150 °C for three days. After the mixture was cooled to room temperature at a rate of 5 °C/h, yellow crystals of **1** were obtained with a yield of 67%, based on cadmium. Anal. Calcd. for $\text{C}_{23}\text{H}_{16}\text{Cd}_2\text{N}_7\text{O}_6\text{S}$: C, 37.01; H, 2.57; N, 13.14. Found: C, 37.05; H, 2.54; N, 13.16. IR/ cm^{-1} (KBr): 3439m, 3096w, 1600m, 1576s, 1514s, 1440s, 1392s, 1355s, 1289w, 1229w, 1187s, 1154m, 1120m, 1009s, 1033m, 960m, 937w, 813m, 787s, 764m, 734w, 656m, 638m, 591m.

2.2.2. Synthesis of $[\text{Cd}(\text{ppca})_2 \cdot \text{H}_2\text{O}]_n$ (**2**)

A mixture of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (147.6 mg, 0.10 mmol) and H_2ppca (18.9 mg 0.10 mmol) in N,N'-dimethylformamide DMF (2 mL) and water (6 mL) was placed in a Teflon-lined stainless steel vessel (10 mL). The vessel was heated at 120 °C for 72 h, and then cooled

to room temperature at a rate of 5 °C/h, giving the colorless block crystals of **2**. Yield: 62%, based on cadmium. Anal. Calcd. for $\text{C}_{18}\text{H}_{12}\text{CdN}_6\text{O}_5$: C, 42.66; H, 2.78; N, 16.58. Found: 42.61; H, 2.80; N, 16.54. IR/ cm^{-1} (KBr): 3439m, 1614s, 1553m, 1436s, 1411s, 1355s, 1276w, 1171w, 1050m, 1016m, 975s, 854m, 812s, 786s, 694m, 653m.

2.2.3. Synthesis of $[\text{Mn}(\text{Hppca})_2 \cdot \text{H}_2\text{O}]_n$ (**3**)

Polymer **3** was synthesized from a mixture of H_2ppca (18.9 mg 0.10 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (19.7 mg, 0.10 mmol), NaOH (8.0 mg, 0.2 mmol) and H_2O (8 mL), which was sealed in a Teflon-lined stainless steel vessel (25 mL), and heated to 170 °C for three days, followed by cooling to room temperature at 5 °C/h. Colorless crystals of **3** were collected. The yield of the product **3** was 57%, based on manganese. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{MnN}_6\text{O}_5$: C, 48.12; H, 3.14; N, 18.71. Found: C, 48.15; H, 3.11; N, 18.69. IR/ cm^{-1} (KBr): 3436m, 1618s, 1553w, 1437s, 1412s, 1354s, 1173w, 1151w, 1050m, 1016w, 975m, 853w, 809m, 787s, 696w, 634w, 564m, 501m.

2.2.4. Synthesis of $[\text{Zn}_2(\text{ppca})_2]_n$ (**4**)

The procedure was the same as that for polymer **4** except that $\text{Zn}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ (20.7 mg, 0.10 mmol) was used instead of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (19.7 mg, 0.10 mmol). colorless block crystals were obtained in 71% yield, based on zinc. Anal. Calcd. for $\text{C}_{18}\text{H}_{10}\text{N}_6\text{O}_4\text{Zn}_2$: C, 42.80; H, 2.00; N, 16.64. Found: C, 42.77; H, 2.03; N, 16.64. IR/ cm^{-1} (KBr): 3423m, 1602s, 1569w, 1507w, 1445s, 1395m, 1341s, 1225w, 1158w, 1038m, 984m, 827m, 777s, 644m.

2.2.5. Synthesis of $[\text{Cu}(\text{ppca})]_n$ (**5**)

Polymer **5** was synthesized hydrothermally in a Teflon-lined stainless steel container by heating a mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.0 mg, 0.10 mmol) and H_2ppca (18.9 mg 0.10 mmol) in N,N-dimethylformamide DMF (2 mL) and distilled water (6 mL) at 150 °C for 3 days. After the mixture was cooled to room temperature at a rate of 5 °C/h, dark green crystals of **5** were obtained with a yield of 69%, based on copper. Anal. Calcd. for $\text{C}_9\text{H}_5\text{CuN}_3\text{O}_2$: C, 43.12; H, 2.01; N, 16.76. Found: C, 43.18; H, 2.12; N, 16.68. IR/ cm^{-1} (KBr): 3441m, 1610s, 1516m, 1454m, 1445s, 1396m, 1331m, 1286s, 1162w, 1111w, 1074m, 1044m, 991m, 814w, 797m, 776s, 637w.

Table 1
Crystal data and structure refinement for polymers **1–5**.

Polymers	1	2	3	4	5
Formula	$\text{C}_{23}\text{H}_{16}\text{Cd}_2\text{N}_7\text{O}_6\text{S}$	$\text{C}_{18}\text{H}_{12}\text{CdN}_6\text{O}_6$	$\text{C}_{18}\text{H}_{12}\text{MnN}_6\text{O}_5$	$\text{C}_{18}\text{H}_{10}\text{N}_6\text{O}_4\text{Zn}_2$	$\text{C}_9\text{H}_5\text{CuN}_3\text{O}_2$
Fw	746.31	520.74	447.28	505.06	250.70
Temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	C_2/c	C_2/c	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	12.027(2)	14.662(3)	14.286(3)	9.386(2)	7.955(2)
<i>b</i> (Å)	22.431(5)	10.262(2)	10.500(2)	13.127(3)	13.866(3)
<i>c</i> (Å)	8.895(2)	12.554(3)	12.746(3)	14.773(3)	7.489(2)
α (deg)	90	90	90	90	90
β (deg)	98.26(3)	107.72(3)	107.03	98.64	94.40
γ (deg)	90	90	90	90	90
<i>V</i> (Å ³)	2374.9(8)	1799.3(6)	1828.1(7)	1799.5(6)	823.6(3)
<i>Z</i>	4	4	4	4	4
<i>D_c</i> (g cm ⁻³)	2.087	1.863	1.625	1.864	2.022
<i>F</i> (0 0 0)	1464	1000	908	1008	500
θ range for data collection (deg)	1.94–27.92	3.24–27.43	2.45–27.96	2.09–27.86	3.10–27.43
Reflections collected/unique	19,541/5648	7151/3687	7992/2179	14,682/4279	6518/1871
Data/restraints/params	5648/0/356	3687/2/271	2179/0/141	4279/0/271	1871/0/136
Goodness-of-fit on <i>F</i> ²	1.079	1.034	1.182	1.103	1.091
Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b	0.0336, 0.0767	0.0308, 0.0826	0.0803, 0.1740	0.0446, 0.0994	0.0403, 0.0951

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)|^2 / \sum w|F_o|^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Download English Version:

<https://daneshyari.com/en/article/1307409>

Download Persian Version:

<https://daneshyari.com/article/1307409>

[Daneshyari.com](https://daneshyari.com)