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Structures and magnetic properties of 3D manganese(II)- and 2D pillar-layered copper(II)-organic framework derived from mixed carboxylate ligands

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ABSTRACT

Two new metal–organic frameworks $[Mn_3(MMA)_2(INA)_2]_n$ (**1**) and $[Cu_2(FA)(INA)_3(H_2O)]_n$ (**2**, FA = formate) were prepared solvothermally by using mixed methylmalonic acid (H_2MMA) and isonicotinic acid (HINA) as the initial reactants. Single-crystal X-ray diffraction analyses reveal that complex **1** has a 3D framework structure consisting of 2D $[Mn_3]$ layer units and INA connector, and **2** owns a 2D pillar-layered structure constituted of mononuclear-Cu(II)-based 2D layer unit and paddle-wheel dinuclear Cu(II) cluster-based pillared linker, which further interspersed with each other to form a 3-fold interpenetrated framework with a $(4^8.6^2)$-*SP* topology. The magnetic studies show that **1** displays antiferromagnetic ordering at low temperature, and a strong antiferromagnetic interaction exists in **2**.

1. Introduction

In the last decades, the rational design and synthesis of magnetic metal–organic frameworks (MMOFs) have attracted considerable interest not only due to their fascinating variety of topological structures but also to their potential for unique properties in the fields of coordination and material chemistry [1–3]. MMOFs bear a visualized crystal structure and can facilitate to clarify magnetic phenomena, reveal magnetostructural correlations and design new magnetic materials exhibiting various magnetic behaviors, such as ferromagnetism, antiferromagnetism, spin canting, metamagnetism and/or single-chain magnetic (SCM) behaviors [4–6]. However, it is still a challenge to control the structural and functional characteristics of MMOFs during the self-assembly syntheses, because many factors may affect the results, such as the coordination geometry of metal ions, connectivity of organic building blocks, reaction conditions (temperatures, solvents, pH values and so on) and presence of auxiliary ligands [7–12]. Therefore, to achieve desired structures with interesting magnetic properties, the choice of appropriate bridging ligands and metal ions is of great importance [3,13].

Up to now, the majority of magnetic frameworks are focused on the first row transition metals (such as Mn and Cu) complexes, because they have an adjustable spin quantum number and are cost-effective [3,14,15]. When the ligand is concerned, the use of mixed flexible small-size and rigid multidentate organic ligands containing carboxylate groups may be a promising strategy to construct such materials. On the one hand, the carboxylate group in the flexible and small-size organic ligand can adopt versatile bridging modes and mediate the magnetic coupling effectively [2,6,16]. On the other hand, the introduction of a rigid ligand as a multidentate linker can be more beneficial to form a porous two-dimensional (2D) or three-dimensional (3D) frameworks, on which the rigid ligand can also confer rigidity and stability [17]. In addition, compared to one ligand, the mixed-ligand strategy may endow MMOFs with more structural diversity and some remarkable physical properties [18]. Flexible and small-size methylmalonic acid and rigid isonicotinic acid both could display various bridging modes and have been demonstrated to be excellent ligands for building MMOFs [19,20]. Herein, by using mixed methylmalonic acid (H_2MMA) and isonicotinic acid (HINA) as the initial reactants, we obtained a 3D manganese(II) magnetic framework, $[Mn_3(MMA)_2(INA)_2]_n$ (**1**), and a 3-fold interpenetrated 2D pillar-layered copper(II) magnetic framework, $[Cu_2(FA)(INA)_3(H_2O)]_n$ (**2**, FA = formate). They exhibit antiferromagnetic ordering at low temperature and strong antiferromagnetic interaction, respectively.

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2. Experimental

2.1. Materials and physical measurements

All chemicals were obtained from commercial sources and used without further purification. FT-IR spectra were recorded in the range of 4000–400 cm^{-1} on a JASCO FT/IR-430 spectrometer with KBr pellets. Elemental analyses were determined by a Vario EL III elemental analyzer. Powder X-ray diffraction (PXPD) measurements were carried out on a Bruker D8 ADVANCE X-ray Diffractometer using Cu Kα ($\lambda = 1.5418$ Å) at room temperature. Thermogravimetric analyses were performed under a flow of nitrogen (40 mL/min) at a ramp rate of 10 °C/min, using a NETZSCH STA 449F3 instrument. Magnetic measurements were performed on a Quantum Design SQUID magnetometer MPMS XL-7. The data were corrected for the sample holder and the diamagnetic contributions.

2.2. Synthesis of 1

0.5 mL of a $MnCl_2$ (1 M, 0.5 mmol) aqueous solution, 0.5 mL of a H_2MMA (1 M, 0.5 mmol) aqueous solution, 0.062 g HINA (0.5 mmol) and 2 mL deionized water were placed in a 15 mL vial. 0.1 M NaOH aqueous solution was added dropwise to adjust the pH value of the resulting solution to about 3.5 under stirring. The vial was sealed and heated at 90 °C in an oven for 48 h, then cooled to room temperature. Colourless block crystals of the products were collected. $[Mn_3(MMA)_2(INA)_2]_n$ (**1**): Yield, 78% based on H_2MMA. Anal. Calcd. for $C_{20}H_{16}Mn_3N_2O_{12}$: C, 37.46; H, 2.52; N, 4.37%. Found: C, 37.51; H, 2.56; N, 4.29%. IR (KBr pellet, cm^{-1}): 2986 w, 2938 w, 1610 s, 1566 s, 1421 s, 1319 s, 1284 m, 1122 w, 1058 w, 1007 w, 912 w, 852 w, 767 m, 681 m, 558 w.

2.3. Synthesis of 2

0.2 mL of a $Cu(NO_3)_2$ (1 M, 0.2 mmol) aqueous solution, 0.4 mL of a H_2MMA (1 M, 0.4 mmol) aqueous solution, 0.025 g HINA (0.2 mmol), 2 mL deionized water and 2 mL DMF were placed in a 15 mL vial. 0.1 M NaOH aqueous solution was added dropwise to adjust the pH value of the resulting solution to about 3.0 under stirring. The vial was sealed and heated at 100 °C in an oven for 48 h, and then blue block crystals of the products were collected. $[Cu_2(FA)(INA)_3(H_2O)]_n$ (**2**): Yield, 56% based on HINA. Anal. Calcd. for $C_{19}H_{15}Cu_2N_3O_9$: C, 41.02; H, 2.72; N, 7.55%. Found: C, 41.12; H, 2.65; N, 7.59%. IR (KBr pellet, cm^{-1}): 3352 s, 3082 w, 1627 s, 1559 m, 1379 s, 1233 w, 1147 w, 1062 m, 852 w, 775 m, 697 m, 558 w, 468 w.

2.4. X-ray crystallography

Crystallographic data were collected on a Bruker D8 Quest CMOS area detector system with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Data reduction and unit cell refinement were performed with Smart-CCD software. The structures were solved by direct methods and refined by full-matrix least squares methods using SHELXL-2016 [21]. For **1** and **2**, all non-hydrogen atoms were refined anisotropically except O3 in **1**, which is disordered and the occupy factors are 0.48(1) and 0.52(1) for O3A and O3B, respectively. Hydrogen atoms on organic ligands were placed in idealised positions and refined using a riding model. Hydrogen atoms on the terminal coordinated molecules were initially found on Fourier difference maps and then restrained by using the DFIX instruction. A summary of the important crystal and structure refinement data of **1** and **2** were given in Table 1. Selected bond lengths and angles for **1** and **2** were listed in Tables S1 and S2, respectively.

Table 1
Crystal data and structure refinement of **1** and **2**.

	1	**2**
Formula	$C_{20}H_{16}Mn_3N_2O_{12}$	$C_{19}H_{15}Cu_2N_3O_9$
Mr.	641.17	556.42
T (K)	293(2)	299(2)
Cryst. system	Monoclinic	Orthorhombic
Space group	*C*2/*m*	*Cmca*
a/Å	17.6606(14)	26.9594(14)
b/Å	6.9124(5)	12.0086(6)
c/Å	9.3741(7)	12.0086(6)
α/°	90	90
β/°	110.327(5)	90
γ/°	90	90
V (Å^3)	1073.10(14)	4171.1(4)
Z	2	8
$d_{calcd.}$, g/cm^3	1.984	1.772
μ(mm^{-1})	1.813	2.098
F(000)	642	2240
Reflections collected/unique	12,112/1017	32,195/2439
R(int)	0.0531	0.0473
GOF on F^2	1.048	1.050
$R1$[a]($I > 2\sigma\ (I)$)	0.0436	0.0644
$wR2$[b](all data)	0.1306	0.1698

[a] $R1 = \sum(||F_o|-|F_c||)/\sum |F_o|$.

[b] $wR2 = \{\sum w[(F_o{}^2 - F_c{}^2)]/\sum w[(F_o{}^2)^2]\}^{.5}$.

3. Results and discussion

3.1. Synthesis and physical characterization

The 3D $[Mn_3(MMA)_2(INA)_2]_n$ (**1**) and 3-fold interpenetrated 2D $[Cu_2(FA)(INA)_3(H_2O)]_n$ (**2**) magnetic frameworks were synthesized solvothermally by using mixed H_2MMA and HINA as the initial reactants. Interestingly, no MMA ligand was captured in the structure of **2**, but the absence of H_2MMA during the synthetic process can't give the product. Furthermore, *syn-syn* formate ligand was observed in the structure of **2** unexpectedly, which may come from the decomposition of DMF molecule.

The thermal stabilities of **1** and **2** were examined by thermogravimetric (TG) analysis on the crystalline samples under the N_2 atmosphere from 25 to 800 °C. As shown in Fig. S2, the weight of **1** keeps constant between 25 °C and 390 °C, indicating that **1** is thermal stable even up to 390 °C. Then, the material shows a striking weight loss of 55.89% in the range of 390–505 °C, suggesting complete decomposition of the framework. After 505 °C, the residue with a weight of *ca* 44.11% can be treated as MnO (calculated 47.70%). For **2**, three mass steps are observed in the TG curve. Firstly, the weight loss of **2** is 11.28% in the range of 25–225 °C, which can be attributed to the loss of one coordinated water molecule and one formate ligand for per formula unit (calculated 11.15%). Then, the weight of **2** keep constant between 225 and 255 °C. After 255 °C, the weight loss may be due to the complete decomposition of the framework.

3.2. Crystal structure of 1

Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic *C*2/*m* space group and has a 3D framework structure, consisting of 2D $[Mn_3]$ layer units and INA connector. As shown in Fig. 1a, the asymmetric unit of the structure is only a quarter of the formula and contains one half of Mn1 ion, one fourth of Mn2 ion, one half of MMA ligand and one half of INA ligand. The two independent Mn(II) sites both are six-coordinated and display a distorted octahedral geometry. However, they have distinct different coordination environments. The Mn1 ion has a $\{NO_5\}$ donor set completed by one nitrogen atom (N1B) and five oxygen atoms (O1, O4, O4A, O4C and O4D) from two INA and three MMA ligands, while the Mn2 ion has a $\{O_6\}$ donor set completed by six oxygen atoms (O2,

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