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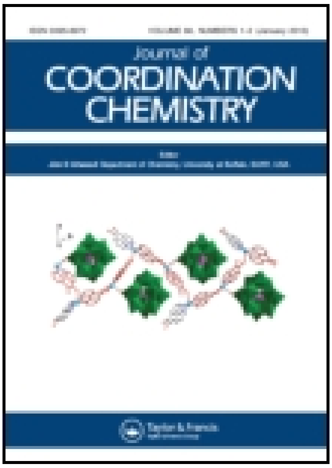

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Two 3-D metal organic frameworks containing 2,2′-bipyridine-5,5′-dicarboxylic acid: synthesis, structure, and magnetic properties

Ming Fang[a], Tao Wang[a], Xulin Lu[a], Aijun Song[a], Li Shen[a] & Hongyan Tian[a]

[a] Department of Chemistry, Hebei Normal University of Science & Technology, Qinhuangdao, PR China

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Two 3-D metal organic frameworks containing 2,2′-bipyridine-5,5′-dicarboxylic acid: synthesis, structure, and magnetic properties

MING FANG*, TAO WANG, XULIN LU, AIJUN SONG, LI SHEN
and HONGYAN TIAN

Department of Chemistry, Hebei Normal University of Science & Technology,
Qinhuangdao, PR China

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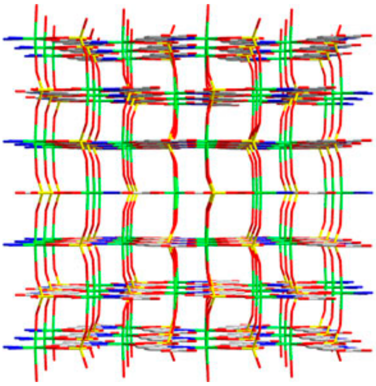

Two metal organic frameworks, $\{[M(H_2BPDC)(SO_4)]\}_n$ (M = Mn (**1**), Zn (**2**)); BPDC = 2,2′-bipyridine-5,5′-dicarboxylic anion), have been synthesized under hydrothermal conditions. The structure analyses of **1** and **2** reveal that the two compounds have similar 3-D structures. Compound **1** crystallizes in the orthorhombic system with space group *Pnma*, while **2** displays a monoclinic system with space group *P21/n*. Magnetic investigation suggests that weak antiferromagnetic coupling exists between adjacent Mn^{2+} ions in **1**.

Keywords: 2,2′-Bipyridine-5,5′-dicarboxylic anion; Manganese; Zinc; MOFs; Antiferromagnetic coupling

Introduction

Crystal engineering plays an important role in the field of materials science and the determination of biological protein structures. The purpose of crystal engineering is to controllably

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*Corresponding author. Email: fangmingchem@163.com synthesize metal organic frameworks (MOFs) based on structure–activity relationships. In the past decades, the design and synthesis of MOFs have attracted interest owing to their versatile applications including luminescence [1], molecular adsorption [2], ion exchange [3], drug delivery [4], catalysis [5], and magnetism [6]. Additionally, MOFs have high crystallinity which can guarantee the homogeneity of the material properties. Many spectacular MOFs have been obtained [1–10]. Ligands play a key role in the design and synthesis of MOFs. Especially, organic multi-carboxylate ligands, such as phthalic acid [7], terephthalic acid [8], trimesic acid [9], and pyridine dicarboxylic acid [10], have been widely used to construct MOFs.

In this contribution, 2,2′-bipyridine-5,5′-dicarboxylic acid (H_2BPDC) [11] was selected as the ligand to fabricate transition metal-based MOFs based on the following considerations: (i) it is a polydentate ligand of up to six donors N_2O_4, displaying various coordination modes; (ii) the higher symmetry of the ligand may cause generation of ordered structures; (iii) the rigidity of the ligand may reduce the possibility of lattice interpenetration in products. Subsequently, two MOFs $\{[M(H_2BPDC)(SO_4)]\}_n$ (M = Mn (**1**), Zn (**2**)); BPDC = 2,2′-bipyridine-5,5′-dicarboxylic anion) were obtained and structurally characterized. The magnetic analyses for **1** indicate the presence of antiferromagnetic exchange between Mn^{2+} ions.

Experimental

Materials and physical measurements

All the chemicals purchased were of reagent grade and used without purification. Water used in the reactions was distilled. The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer elemental analyzer. Magnetic susceptibilities were performed on a Quantum Design PPMS-9 ACMS magnetometer. Diamagnetic corrections were made with Pascal’s constants for all the constituent atoms.

The syntheses of 1 and 2 (3-D)

A mixture of $MnSO_4 \cdot H_2O$ (0.3 mM, 51 mg) for **1** and $ZnSO_4 \cdot 7H_2O$ (0.3 mM, 86 mg) for **2**, H_2BPDC (0.1 mM, 24 mg), H_2O (4 mL), and C_2H_5OH (6 mL) was added in a 25 mL Teflon-lined stainless steel reactor at 140 °C for 2 days, and then slowly cooled to room temperature. Colorless block-like crystals of **1** and **2**, suitable for X-ray data collection, were obtained by filtration, washed by distilled water, and air-dried. Yield: 48 and 28% based on BPDC for **1** and **2**, respectively. Elemental analysis Calcd (%) for $C_{12}H_8MnN_2O_8S$ (**1**): C, 36.47; H, 2.04; N, 7.09. Found: C, 36.39; H, 2.07; N, 7.13. For $C_{12}H_8ZnN_2O_8S$ (**2**): C, 35.53; H, 1.99; N, 6.91. Found: C, 35.46; H, 2.04; N, 6.95.

Crystallographic studies

Single-crystal X-ray diffraction measurements of **1** and **2** were collected at 173 K on a SuperNova Single Crystal Diffractometer equipped with graphite monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å). Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques

Table 1. Crystal data and structure refinement details for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{12}H_8MnN_2O_8S$	$C_{12}H_8ZnN_2O_8S$
Fw	395.21	405.63
Temperature (K)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	*P21/n*
a (Å)	10.949(2)	6.4251(5)
b (Å)	6.5995(13)	10.8881(8)
c (Å)	18.318(4)	18.3449(17)
α (°)	90	90
β (°)	90	97.213(8)
γ (°)	90	90
V (Å^3)	1323.6(5)	1273.20(18)
Z	4	4
D_{Calcd} (g/cm^3)	1.983	2.116
μ (mm^{-1})	1.207	2.147
Total reflns.	10,413	5737
Unique reflns.	1275	5737
Parameters	142	223
θ Range (°)	3.28/25.01	2.90/28.96
F (0 0 0)	796	816
GOF on F^2	1.170	1.042
R_{int}	0.0815	–
R_1/wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0664$ $wR_2 = 0.1126$	$R_1 = 0.0553$ $wR_2 = 0.1489$
R_1/wR_2 (all data)	$R_1 = 0.0828$ $wR_2 = 0.1186$	$R_1 = 0.0652$ $wR_2 = 0.1587$

using SHELXS-97 and SHELXL-97 [12]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogens were placed in idealized positions. Compound **2** is a twin crystal structure, which is split by the software. Crystallographic data for **1** and **2** are summarized in table 1. Selected bond lengths and angles are summarized in table (S1, see online supplementary material at http://dx.doi.org/10.1080/00958972.2014.944175) in Supplemental data.

Results and discussion

Crystal structure of {[M(H_2BPDC)(SO_4)]}$_n$ (M = Mn(1), Zn(2))

X-ray diffraction analysis reveals that **1** crystallizes in the orthorhombic system, space group *Pnma*. Compound **2** is isostructural to **1**; however, different space group *P21/n* (figures S1–S3), and so the structure of **2**, is not commented. The asymmetric unit of **1** consists of one crystallographically independent Mn^{2+}, one BPDC ligand, and one sulfate, as shown in figure 1. The local coordination geometry for the six-coordinate Mn1 is distorted octahedral, which consists of one carboxylic oxygen, two nitrogens, and three oxygens from three sulfate anions. The Mn–O (carboxylic) distance is 2.231(5) Å, Mn–O (sulfate), bond lengths are 2.094(5) and 2.158(4) Å, and the Mn–N bond distances are 2.247(6) and 2.280(6) Å, respectively. The BPDC anion is a bidentate metal linker (scheme 1) with the two nitrogens chelated with one Mn^{2+} and one carboxylic oxygen coordinating with another Mn^{2+}. The sulfate, which acts as a tridentate ligand, plays a rather important role in the construction of

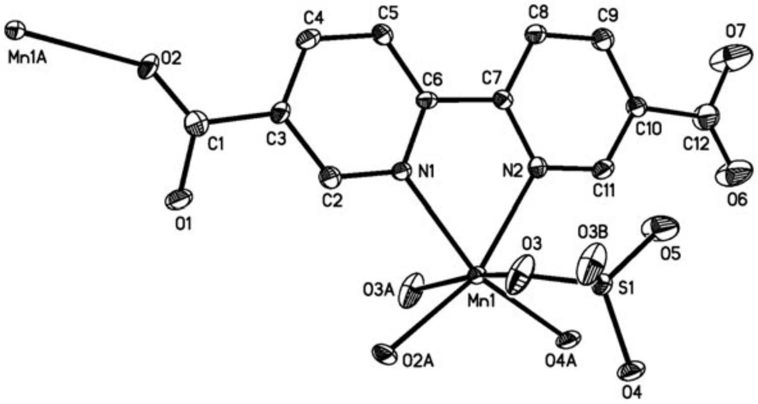


Figure 1. The molecular structure of **1**.

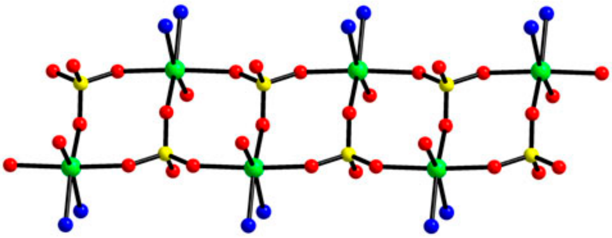


Figure 2. The 1-D chain structure of **1** along the *b* direction.

the structure. The Mn^{2+} is connected to a 1-D ladder-like chain, along the *b* direction by bridging sulfates (figure 2), then the 1-D chain is further connected to a 3-D framework by the ligands (figure 3).

Magnetic properties

The magnetic susceptibilities of **1** were measured on the microcrystalline sample from 2 to 300 K under 1000 Oe field, as shown in figure 4. At room temperature, the $\chi_M T$ value for **1** is 4.15 $cm^3\,K\,M^{-1}$, close to the expected value of 4.38 $cm^3\,K\,M^{-1}$ for one Mn^{2+} ion ($S = 5/2$). On lowering the temperature, the $\chi_M T$ value decreases gradually from 4.15 $cm^3\,K\,M^{-1}$ at 300 K to 3.68 $cm^3\,K\,M^{-1}$ at 50 K, then slumps to a value of 0.4 $cm^3\,K\,M^{-1}$ at 2 K. This behavior may indicate the presence of weak antiferromagnetic coupling between adjacent Mn^{2+} ions. The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) above 10 K obeyed the Curie–Weiss law $1/\chi_M = (T - \theta)/C$ with $C = 4.32$ and Weiss constant $\theta = -9.02$. The negative value of θ further confirms the existence of antiferromagnetic coupling between Mn^{2+} ions [13]. For **1**, the main magnetic interactions may occur between adjacent Mn^{2+} ions bridged by sulfate, whereas the exchange interactions between Mn^{2+} ion bridged through BPDC may be ignored because of the long Mn ⋯ Mn distance; the structure is taken as an infinite-chain model. To estimate the strength of the antiferromagnetic coupling, the equation

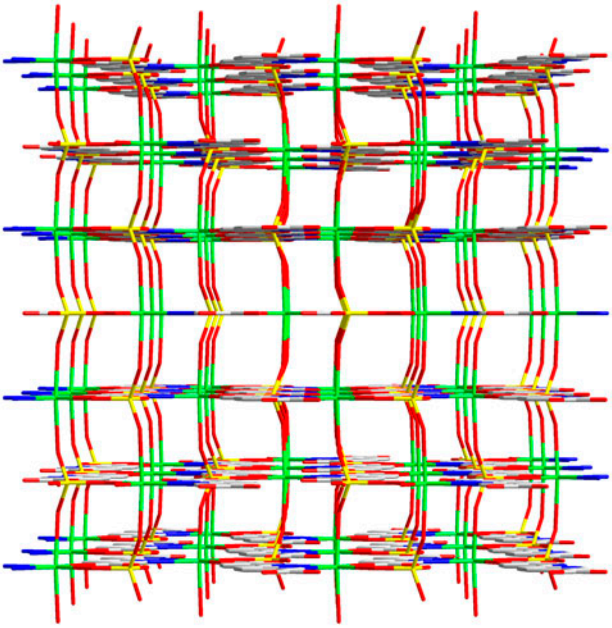


Figure 3. The 3-D framework of **1** along the *c* direction. Color codes: red, O; green, Mn; yellow, S; blue, N (see http://dx.doi.org/10.1080/00958972.2014.944175 for color version).

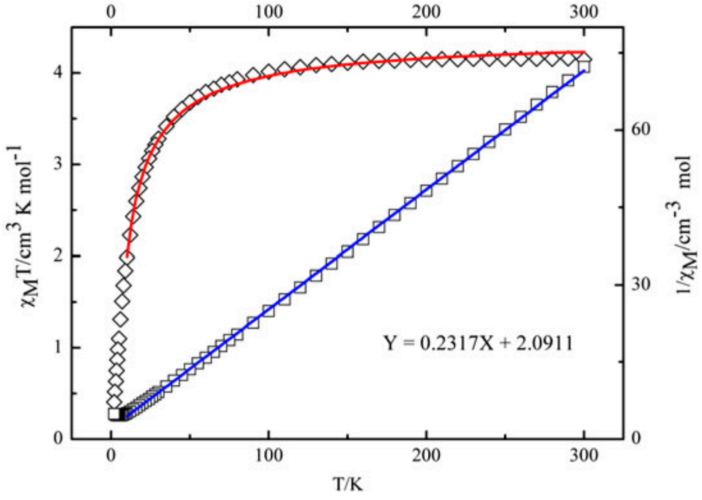
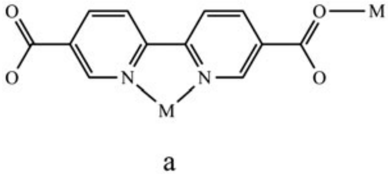


Figure 4. The plots of $\chi_M T$ *vs.* T, $1/\chi_M$ *vs.* T and the linear fit of Curie–Weiss law for **1** under 1000 Oe field.

derived by Fisher with $H = -2J\Sigma S_i S_{i+1}$ as following is applied to fit the magnetic data above 10 K:

$$\chi = \frac{N\beta^2 g^2}{kT} \cdot \frac{A + Bx^2}{1 + Cx + Dx^3} \tag{1}$$



Scheme 1. Coordination modes of BPDC.

$$x = |J|/kT \tag{2}$$

In this equation [14], $A = 2.9167$, $B = 208.04$, $C = 15.543$, $D = 2707.2$; N, g, β, k have their usual meanings; and J is the exchange coupling constant between adjacent Mn^{2+} ions. Based on this equation, the least-squares fitting of magnetic susceptibility data leads to $J = -0.48\,\mathrm{cm}^{-1}$, $g = 2.00$, and the agreement factor R, defined as $R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{Calcd}})^2/\sum(\chi_{\mathrm{obsd}})^2$, is 1.54×10^{-3}. The result indicates very weak antiferromagnetic interaction between Mn^{2+}. Such a weak coupling interaction often occurs through carboxylate bridges in manganese(II) compounds. Zuo *et al.* reported a 3-D manganese-based MOF with a J value of $-0.27\,\mathrm{cm}^{-1}$, and the metal centers bridged in a Mn–O-C-O–Mn model [15]. Hachuła *et al.* reported that a compound with Mn–O-C-O–Mn bridge has a J value of $-0.74\,\mathrm{cm}^{-1}$ [16].

Conclusion

Two 3-D MOFs have been synthesized under hydrothermal conditions and structurally characterized. The magnetic properties reveal that weak antiferromagnetic interaction exists between the adjacent Mn^{2+} ions in **1**.

Acknowledgements

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