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Synthesis, Crystal Structure, and Magnetic Properties of 2D Coordination Polymer $\{[Mn(PDB)(H_2O)_2] \cdot H_2O\}_n$[1]

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Abstract—A coordination polymer $\{[Mn(PDB)(H_2O)_2] \cdot H_2O\}_n$ (**I**) (H_2PDB = pyridine-3,4-dicarboxylic acid) was hydrothermally synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction. The crystal of complex **I** are triclinic: $C_7H_9NMnO_7$, $M = 274.09$; $a = 7.2389(18)$, $b = 8.045(2)$, $c = 9.157(2)$ Å, $\alpha = 75.421(12)°$, $\beta = 68.092(9)°$, $\gamma = 76.021(12)°$, $V = 1472.3(2)$ Å^3, $Z = 2$, $\rho_c = 1.927$ g/cm^3, $\mu = 1.420$ mm^{-1}, space group $P\bar{1}$, $F(000) = 278$, $R = 0.0253$ and $wR = 0.0621$ for 1709 observed reflections ($I > 2\sigma(I)$). X-ray diffraction structure analyses reveal that two-dimensional layers were formed as bridged by PDB, and further assembled into the three-dimensional framework supramolecular structure via hydrogen bonding interaction. Magnetic susceptibility measurements reveal an antiferromagnetic interaction in **I**.

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INTRODUCTION

Hydrothermal synthesis of metal organic framework (**MOF**) structures is an area of intense research activity, because MOF have potential applications as electronic, magnetic, optical, absorbent, and catalytic materials [1–7]. MOF could be directly constructed by coordination bonds using transition metal ions and multifunctional ligands [8, 9]. So, as bridging ligands, carboxylates, especially multicarboxylates are of immense interest in the construction of MOF owing to the fact that these ligands have several characteristics: the first is that the carboxylate groups may be completely or partially deprotonated, resulting in rich different coordination mode [10]. The second is that the steric orientation of some carboxylate groups is flexible, so it can appreciably rotate and connect metal ions in different directions to form high-dimensional frameworks with the metal atom [11]. Many of MOF containing symmetrical multicarboxylate ligands, such as 1,3,5-benzenetricarboxylate, and pyridine-2,6-dicarboxyate, have been used by Yaghi or other research groups in the construction of the 2D or 3D structure with nanoporous pores [12,13]. In contrast, as a member of unsymmetrical multicarboxylate ligands, the conjugation interaction of pyridine-3,4-dicarboxylic acid (**H_2PDB**) between the pyridine group and carboxyl group is markedly weakened because of steric hidrance between the two adjacent carboxyl groups. Therefore, H_2PDB is likely to form high-dimensional frameworks with metal atoms [14, 15].

In this paper, we report a metal organic coordination polymer $\{[Mn(PDB)(H_2O)_2] \cdot H_2O\}_n$ (**I**). Compound **I** exhibits two-dimensional layer structure constructed by Mn(II) and PDB ligands, which are further assembled into three-dimensional framework supramolecular structure via the abundant hydrogen bonding interaction. Magnetic measurements show that an antiferromagnetic interaction occurs in **I**.

EXPERIMENTAL

Reagent and Physical Measurements. All chemicals were of regent grade quality obtained from commercial sources and used without further purification. C, H, N analyses were carried out with a Finnigan EA1112 element analyzer. IR spectra were performed on a Nicolet 470 spectrometer with KBr pellets in the 4000–400 cm^{-1} regions. The magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design MPMS-XL-5 SQUID magnetometer in the temperature range 2–300 K and magnetic field up to 5 T. Diamagnetic corrections were estimated from Pascal's constants. The determination of the crystal was recorded on a Rigaku Saturn CCD area-detector diffractometer.

Synthesis I. A mixture of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.05 mmol, 0.012 g), H_2PDB (0.3 mmol, 0.050 g), and water (12 ml) was stirred for 20 min in air. The mixture was then transferred to a 23 ml teflon reactor and kept at 120°C for 3 days under autogenous pressure, and then cooled to room temperature at a rate of 5°C/h. Purple crystals of **I** were obtained and washed with deion-

[1] The article is published in the original.

Selected bond lengths and bond angles for $\{[Mn(PDB)(H_2O)_2] \cdot H_2O\}_n^*$

Bond	*d*, Å	Bond	*d*, Å
Mn(1)–O(1)$^{\#1}$	2.0901(14)	Mn(1)–O(3)$^{\#3}$	2.2676(14)
Mn(1)–O(6)	2.1683(15)	O(3)–C(7)	1.263(2)
Mn(1)–O(4)$^{\#2}$	2.2021(13)	O(2)–C(6)	1.245(2)
Mn(1)–N(1)	2.2388(15)	O(1)–C(6)	1.257(2)
Mn(1)–O(5)	2.2462(14)		
O(4)–C(7)	1.258(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)$^{\#1}$Mn(1)O(6)	97.33(6)	O(1)$^{\#1}$Mn(1)O(4)$^{\#2}$	90.16(6)
O(6)Mn(1)O(4)$^{\#2}$	86.97(5)	O(1)$^{\#1}$Mn(1)N(1)	96.40(6)
O(6)Mn(1)N(1)	92.32(6)	O(4)$^{\#2}$Mn(1)N(1)	173.44(5)
O(1)$^{\#1}$Mn(1)O(5)	173.06(6)	O(6)Mn(1)O(5)	88.41(6)
O(4)$^{\#2}$Mn(1)O(5)	86.25(5)	N(1)Mn(1)O(5)	87.22(5)
O(1)$^{\#1}$Mn(1)O(3)$^{\#3}$	92.23(6)	O(6)Mn(1)O(3)$^{\#3}$	169.82(5)
O(4)$^{\#2}$Mn(1)O(3)$^{\#3}$	89.52(5)	N(1)Mn(1)O(3)$^{\#3}$	90.08(5)
O(5)Mn(1)O(3)$^{\#3}$	81.82(5)		

* Symmetry code: $^{\#1}$ $x-1, y, -z$; $^{\#2}$ $x-1, y+1, z$; $^{\#3}$ $-x+1, -y, -z+1$.

ized water and absolute ethanol (the yield was 66% based on Mn). IR spectrum (ν, cm^{-1}): 3419 s, 1627 s, 1595 s, 1572 s, 1497 m, 1418 s, 1229 w, 1173 w, 840 m, 779 s, 712 m.

For $C_7H_9NO_7Mn$

anal. calcd, %:	C, 30.67;	H, 3.31;	N, 5.11.
Found, %:	C, 30.65;	H, 3.30;	N, 5.08.

X-Ray Structure Determination. A purple single crystal with dimensions of $0.20 \times 0.20 \times 0.20$ mm was selected and the determination of the crystal was carried out on a Siemens Smart CCD diffractometer with a molybdenum-monochromate MoK_α radiation ($\lambda = 0.71073$ Å). The crystal of complex I are triclinic: $C_7H_9NMnO_7$, $M = 274.09$; $a = 7.2389(18)$, $b = 8.045(2)$, $c = 9.157(2)$ Å, $\alpha = 75.421(12)°$, $\beta = 68.092(9)°$, $\gamma = 76.021(12)°$, $V = 1472.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.927$ g/cm^3, $\mu = 1.420$ mm^{-1}, space group $P\bar{1}$.

Intensity data were obtained in a range of $3.07° \le \theta \le 27.44°$ at 293(15) K by using an ω-scan technique. The corrections for the LP factor and empirical absorption correction were applied. The structure was resolved by a direct method. All the collected points were used in the structure analysis. All the non-hydrogen atoms were determined with successive difference Fourier syntheses and refined with anisotropic thermal parameters by full-matrix least-squares of F^2. All hydrogen atoms were located at the calculated positions. All calculations were performed on a computer with the SHELX-97 program package [16, 17]. The final refinement converged at $R = 0.0253$ and $wR = 0.0621$ ($w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 1709 observed reflections with $I > 2\sigma(I)$; $S = 0.986$, $(\Delta\rho)_{max} = 0.371$ and $(\Delta\rho)_{min} = -0.319$ e Å^{-3}.

The atomic coordinates and other parameters of structure I have been deposited with the Cambridge Crystallographic Data Center (no. 672330; deposit@ccdc.cam.ac.uk).

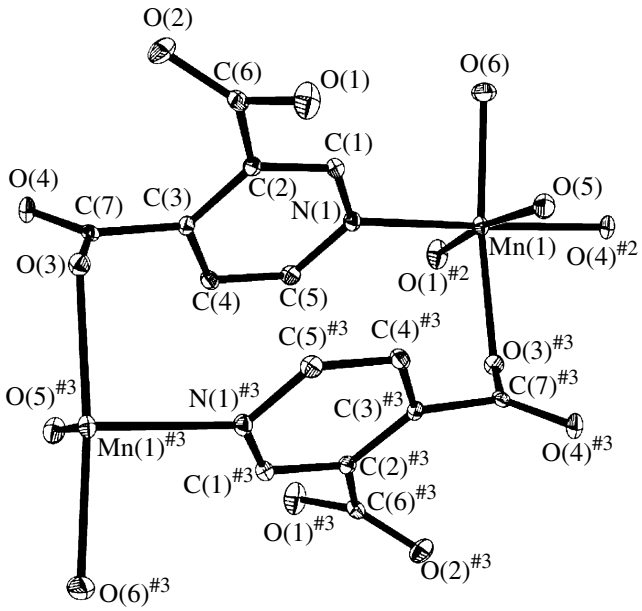

Fig. 1. ORTEP representation (30% thermal probability ellipsoids) of the crystal structure **I** $^{\#2}$ $x-1, y+1, z$; $^{\#3} = -x+1, -y, -z+1$.

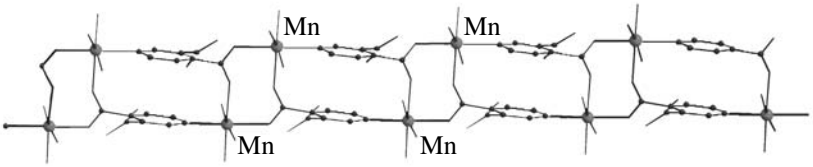

Fig. 2. 1D chain of **I** along the *x* axis.

RESULTS AND DISCUSSION

Selected bond lengths are given in table. The molecular structure of the title complex is shown in Fig. 1. In **I**, Mn(II) atoms were coordinated by three oxygen atoms from three PDB ligands (Mn(1)–O(1)$^{\#1}$ 2.0901, Mn(1)–O(4)$^{\#2}$ 2.2021, Mn(1)–O(3)$^{\#3}$ 2.2676 Å), two oxygen atoms from two coordinated water molecules (Mn(1)–O(5) 2.2462, Mn(1)–O(6) 2.1683 Å), one nitrogen atom from four PDB ligands (Mn(1)–N(1) 2.2388 Å). In detail, O(1)$^{\#1}$, O(3)$^{\#3}$, O(5), and O(6) locate at the equatorial plane, they and Mn(1) are almost coplanar. N(1) and O(4)$^{\#2}$ occupy the axial positions. It should be noted that in **I** the PDB adopts a novel monodentate-bidentate μ^4-coordination fashion versus two CO_2 groups (O(1)–C(6)–O(2) monodentate; O(3)–C(7)–O(4) bidentate) and differ from the PDB ligands adopting bidentate μ^5-coordination fashion in the coordination polymer $[Cd_3(PDB)_2(OH)(H_2O)_2]_n$ which reported by Wang et al. [11]. In some lanthanide metal coordination polymers, the nitrogen atom of PDB ligands even did not participate in coordination [14]. The crystallographically equivalent Mn(II) atoms were linked by the O–C–O bridge of 4-position carboxyl group to form a dimeric unit, the dimeric unit was further linked by the pyridine ring to form a ID chain along the *x* axis (Fig. 2), and all Mn(II) in this chain are perfectly coplanar. The adjacent chains were connected by 3-position carboxyl group to construct a novel 2D layer as shown in Fig. 3.

In addition, there are four types of hydrogen bonding interaction in **I**. The first is intermolecular hydrogen bonding that exists in the oxygen atoms of coordinated water and the lattice water (O(6)···O(7)$^{\#1}$ 2.797(2) Å, O(6)–H(6*B*)···O(7)$^{\#1}$ 172°, (O(5)···O(7) 2.799(2) Å, O(5)–H(5*A*)···O(7) 173°). The second is intermolecular hydrogen bonding between the oxygen atoms of coordinated water and oxygen atoms of the carboxyl group (O(5)···O(3)$^{\#2}$ 2.747(19) Å, O(5)–H(5*B*)···O(3)$^{\#2}$ 167°, (O(5)···O(4)$^{\#2}$ 3.041(2) Å, O(5)–H(5*B*)···O(4)$^{\#2}$ 113°, O(6)···O(2) 2.770 Å, O(6)–H(6*A*)···O(2) 160°). The third is intermolecular hydrogen bonding between the oxygen atoms of lattice water and oxygen atoms of the carboxyl group (O(7)···O(2)$^{\#2}$ 2.749(19) Å, O(7)–H(7*B*)···O(2)$^{\#2}$ 164°, O(7)···O(4) 2.887(2) Å, O(7)–H(7*A*)···O(4) 170°). The abundant hydrogen bonding result in the layers being extended into 3D supramolecular frameworks (Fig. 4).

The temperature dependence of the magnetic susceptibilities for compound **I** is measured under an applied field of 1000 Oe in the temperature range 2–300 K. The result is shown in the forms of χ_M–T_{plot} (Fig. 5). The up value per Mn_2 at 300 K is 6.43 μ_B, which is larger than the spin-only value of the high-spin Mn^{2+} ion (5.92 μ_B, $S = 5/2$). The compound can be considered as a complex with a binuclear unit as a building block and

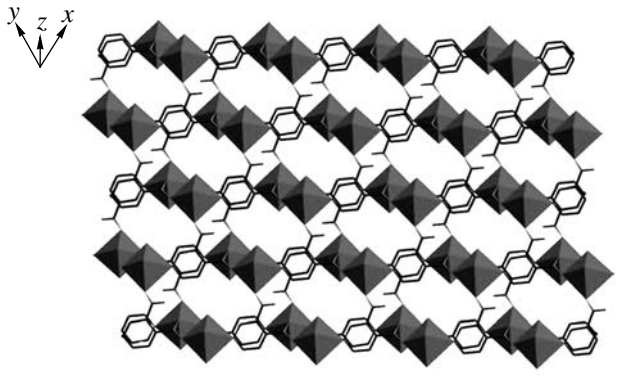

Fig. 3. 2D network structure of **I**.

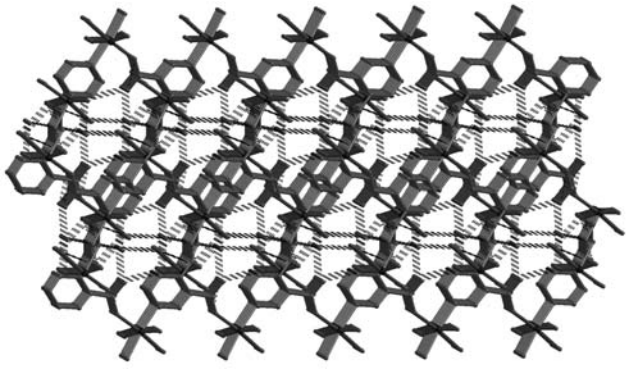

Fig. 4. View of the 3D supramolecular framework of **I**.

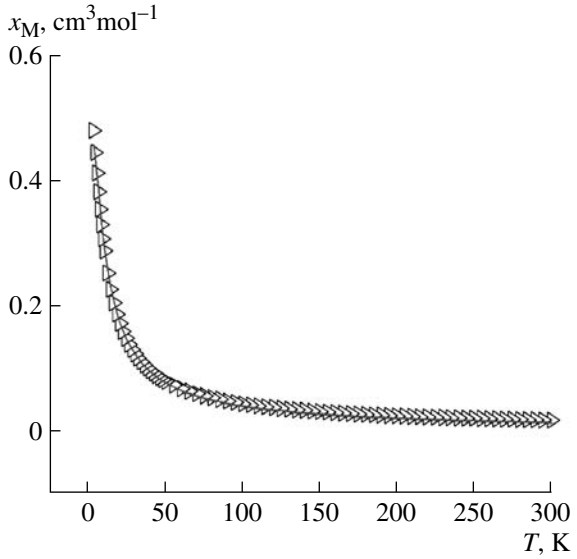

Fig. 5. Plots of $\chi_M - T$. The open points are the experimental ones, and the red solid line corresponds to the best fit obtained.

the Mn···Mn distance is 4.805 Å. The result shows that an antiferromagnetic interaction occurs in **I**. The magnetic data were fitted using the expression as below:

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \times \frac{e^{2JIkT} + 5e^{6JIkT} + 14e^{12JIkT} + 30e^{20JIkT} + 55e^{30JkT}}{1 + 3e^{2JIkT} + 5e^{6JIkT} + 7e^{12JIkT} + 9e^{20JIkT} + 11e^{30JIkT}}$$

and the exchange interaction between the binuclear units may be treated as follows:

$$\chi = \frac{\chi_M}{1 - (2zJ'/Ng^2\beta^2)\chi_M},$$

which is the intermolecular change zJ' by a molecular field model. The best fit parameters are $g = 1.94$, $J = -0.31$, $zJ' = -0.030$, Chi^2/GOF = 0.00002, $R^2 = 0.99822$.

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