A new manganese coordination polymer involving *in situ* generated formate

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ABSTRACT

A new three-dimensional (3D) manganese coordination polymer, $[Mn_2(IP)_{1.5}(HCOO)(DEF)]_n$ (**1**) (H_2IP = isophthalic acid, DEF = N,N-diethylformamide), has been solvothermally synthesized in DEF. X-ray single crystal structural data reveal that compound **1** crystallizes in orthorhombic space group *Fdd*2 and was constructed with infinite zig-zag chains of corner- and edge-sharing octahedral $(MnO_6)_n$ units interconnected by isophthalate to form a 3D framework. The *in situ* generated formate ions from the hydrolysis of DEF adopt a special bridging mode to build the secondary building units (SBUs). Variable-temperature magnetic susceptibility of compound **1** exhibits overall weak antiferromagnetic coupling between the adjacent Mn^{2+} ions.

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1. Introduction

Coordination polymers (CPs) have been received growing interest recently because of their intriguing architectures and potential applications as functional materials in gas adsorption, separation, sensor, drug delivery, catalysis, and magnetism [1–7]. Traditionally, CPs are obtained by reactions of pre-synthesized or commercially available ligands with metal ions. The solvo/hydrothermal method has been widely used to synthesize CPs since it can settle the problems of ligands solubility and improve the reactivity of reactants in the crystallization process [8]. The preparation of CPs could be affected by several factors, including the coordination nature of the metal ion, ligand, solvent, temperature, and so on [9,10]. Among those mentioned above, the selection of ligand is crucial in the construction of coordination polymers because changing ligand can control and regulate the topologies of coordination polymers [11]. Among a multitude of organic ligands, aromatic dicarboxylic acid ligands are excellent structural linkers since they are effective bridging ligands with four coordinating oxygen atoms from two carboxylate groups and their phenyl groups can function as mediator for transmitting exchange interaction between paramagnetic metal centers [12,13]. A typical aromatic polycarboxylate ligand, isophthalic acid (H_2IP) has been widely used to construct CPs [14–16]. Meanwhile the formate

ion, as the simplest, smallest and rigid carboxylate, and possibly adopting various bridging modes, has been employed to construct quite a lot CPs [17–23]. In addition to its similarity to azides in mediating magnetic coupling, many formate-containing CPs also have nanoporous channels with promising gas-sorption properties [17–19,24–26]. The search of new organic ligands with different coordination habits is still a fundamental task for the crystal engineering of coordination polymers. There is also current interest in CPs containing paramagnetic metal ions, driven by potential applications as molecule-based magnetic materials [27–33]. As part of our ongoing research work on CPs of dicarboxylates, several metal carboxylates with interesting magnetic properties have been successfully prepared [16,34]. Such interesting results have intrigued us to continue to explore the construction of coordination polymers based on manganese. As a functional metal center, manganese is attracting more and more attention due to its ability to function as progenitor of novel magnetic molecular materials [20–23,35,36]. Herein a new 3D coordination polymer, $[Mn(IP)_{1.5}(HCOO)(DEF)]_n$ (**1**) (DEF = N,N-diethylformamide) with *in situ* generated formate is presented. Its synthesis, crystal growth, structural characterization and magnetic properties are also discussed.

2. Experimental

2.1. Material and general methods

Compound **1** was synthesized from a solvothermal one-pot reaction of $MnCl_2·4H_2O$ and H_2IP in DEF solution at 150 °C for

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5 d. All the materials of reagent grade were purchased from commercial sources and used without further purification. A mixture of H_2IP (0.2 mmol, 0.0332 g), $MnCl_2 \cdot 4H_2O$ (0.25 mmol, 0.0612 g) and DEF (5 mL) was placed in a 25 mL Teflon-lined stainless steel vessel and was stirred at room temperature for 5 min. The mixture was then heated at 150 °C for 5 d, followed by slowly cooling down to room temperature at a rate of 10 °C/h. Light yellow crystals of $[Mn(IP)_{1.5}(HCOO)(DEF)]_n$ were collected through filtration and washed with distilled water and ethanol for several times. The product yield was 40% in weight based on manganese. Elemental analysis (C, H and N) was carried out with a Vario EL elemental analyzer. *Anal.* Calc. for $C_{18}H_{18}Mn_2NO_9$: C, 43.01; H, 3.58; N, 2.79. Found: C, 43.13; H, 3.49; N, 2.87%. FT-IR spectra (KBr) were recorded in the range of 4000–400 cm^{-1} on a Bruker IFS 66v/S Fourier-transform infrared spectrometer. FT-IR (KBr, cm^{-1}): 1658 s, 1611 s, 1562 s, 1402 vs 1210 w, 943 vw, 831 w, 781 w, 758 s, 718 s, 658 s, 451 s.

2.2. Characterization

Single crystal X-ray diffraction measurements was carried out on a Rigaku Mercury CCD at 293 K, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Powder X-ray diffraction (PXRD) measurement was conducted on a Rigaku diffractometer using Cu Kα (λ = 1.5406 Å) radiation. The structure was solved with direct methods (SIR 97) and refined anisotropically with the full-matrix least-squares method on F^2. The hydrogen atoms were generated geometrically. All calculations were carried out on a SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation. Relevant data about the collections and structure solutions are summarized in Table 1.

Thermal gravimetric analysis (TGA) was carried out to examine the thermal stability of compound **1** using a thermogravimetric analyzer (Perkin-Elmer TGA7) at 10 °C/min from 40 to 800 °C under nitrogen flow. Direct current (dc) magnetic measurement for powder crystalline compound **1** was made on a Quantum Design MPMS-XL SQUID magnetometer in the temperature range of 2–300 K with an applied field of 10 kOe. Samples were packed in a gelatin capsule for the measurements. Magnetic susceptibility of the gelatin capsule was subtracted from the raw data. Diamagnetic susceptibility of the sample was corrected with the conventional Pascal method.

3. Results and discussion

Fig. 1 shows the FT-IR transmission spectrum of compound **1**. The strong absorption band at 1659 cm^{-1} is attributed to the asymmetric stretch of carbonyl in DEF and the band at 1611 cm^{-1} is assigned to the asymmetric carboxylate stretch for IP^{2-} and formate. The very strong band at 1402 cm^{-1} can be ascribed to the symmetric stretch of carboxylates.

PXRD pattern was measured to examine the crystallinity of compound **1** (Fig. 2). The diffraction peaks of experimental sample match well with the diffraction pattern simulated from the single crystal data of $[Mn_2(IP)_{1.5}(HCOO)(DEF)]_n$ at corresponding positions, which indicates that the sample contains crystalline $[Mn_2(IP)_{1.5}(HCOO)(DEF)]_n$ with good crystallinity.

It is noteworthy to mention that the formate ion in compound **1** was generated from *in situ* hydrolysis of DEF [37]. Formate provided the necessary building blocks because of its minor steric hindrance and it was closely associated with the kinetics of crystallization [38]. Similar phenomenon with *in situ* hydrolysis
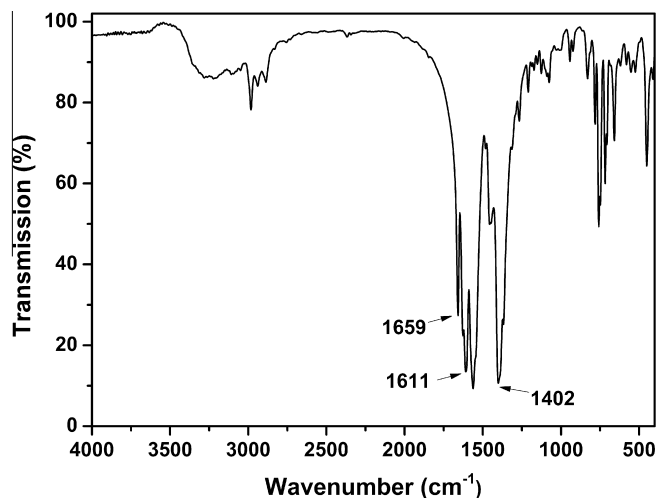

Fig. 1. FT-IR transmission spectrum of compound **1**.

Table 1
Crystal data and structure refinement parameters for **1**.

Structure parameter	1
Empirical formula	$C_{18}H_{18}Mn_2NO_9$
Formula weight	502.21
T (K)	293(2)
λ(Mo Kα) (Å)	0.71070
Crystal system	orthorhombic
Space group	*Fdd*2
a (Å)	39.120(8)
b (Å)	22.963(4)
c (Å)	8.947(2)
V (Å^3)	8037(3)
Z	16
D_{calc} (Mg m^{-3})	1.660
μ (mm^{-1})	1.308
$F(000)$	4079
θ Range for data collection (°)	3.54–27.48
Limiting indices	$-43 \leqslant h \leqslant 50$, $-21 \leqslant k \leqslant 29$, $-11 \leqslant l \leqslant 11$
Reflections collected/unique (R_{int})	15 619/4591(0.0287)
Completeness to θ = 27.48 °	99.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4951/1/276
Goodness-of-fit (GOF) on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0377, wR_2 = 0.1036
R indices(all data)	R_1 = 0.0384, wR_2 = 0.1046

$R = \sum||F_0| - |F_c||\sum|F_0|$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bP]$, where $P = (Max(F_o^2, 0) + 2 F_c^2)/3$, where a = 0.0672 and b = 11.87 for **1**.
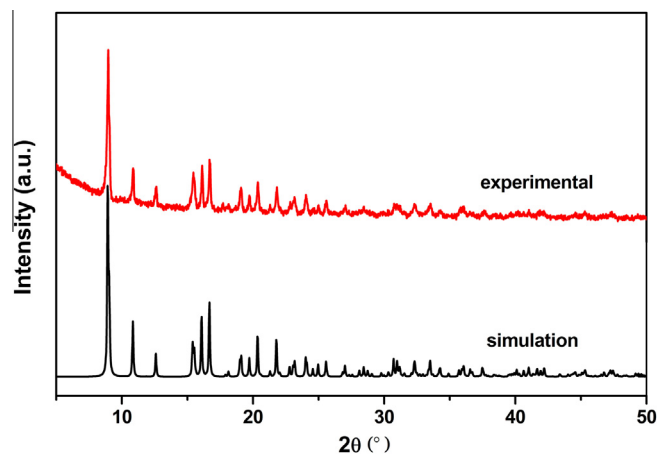
Fig. 2. PXRD pattern of experimental data and simulation result.