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Three Mn(II) complexes based on 6-(3-pyridyl)isophthalic acid ligand: Structure modulation, stability and magnetic properties

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ABSTRACT

Based on the 6-(3-pyridyl)isophthalic acid (H_2pip) ligand, three new complexes [Mn(Hpip)$_2$(bipy)$_2$(H_2O)$_2$] (**1**), {[Mn(pip)(bibp)]·DMA}$_n$ (**2**) and [Mn(pip)]$_n$ (**3**), have been obtained under hydrothermal conditions and characterized by single-crystal X-ray diffraction. Compound **1** reveals a 0D mononuclear structure, and isolated molecules are further linked by hydrogen-bonds into a 3D supramolecular structure. In **2**, the binuclear $Mn_2(COO)_4N_4$ secondary building units (SBUs) are linked by neighboring ligands to result in a 2D layer structure. Inside of the structure of **3**, one-dimensional (1D) chains are formed by the coordination of carboxylate groups and Mn^{2+}, which are further connected by the ligands generating a 3D network. Notably, complex **2** and **3** reveal high thermal and aqueous stability, suggested by TGA and PXRD data. Moreover, the magnetic measurements indicate polymers **2** and **3** are both exhibit antiferromagnetic behavior.

1. Introduction

During the past few decades, the rational design and construction of coordination polymers (CPs) have been widely studied not only due to their fascinating structures and topologies but also the potential applications such as magnetism, gas storage, separation, catalysis, luminescence, ion exchange and so on [1–10]. However, it is still a big challenge to synthesize CPs more predictably and controllably at present, since the self-assembly of frameworks and final structures of polymers could be affected by too many factors, such as solvents, temperatures, pH value of the solution, ligand structures and so on [11–19]. As CPs are commonly obtained through the assembly of various organic ligands and inorganic secondary building units (SBUs, generally metal ions or metal-containing units), the exploitation of proper kinds of ligands is of great importance [20–22]. Among numerous kinds of organic ligands, carboxylate ligands with N-donors has been of specially interest in recent years. Their strong affinities with transitional metal ions and diverse coordination modes make them good candidates to construct CPs with various dimensional structures and interesting properties [23–26]. Our previous work showed that 6-(3-pyridyl)isophthalic acid (H_2pip), as a ligand of this kind, have present various coordination modes and seemed to be a good choice [27].

On the other hand, because of the weak coordination bonding, many CPs are unstable when separated from their mother solution, which could limit their application. Therefore, to make CPs for practical utilization, stability of the framework is one of the key factors that could not be neglected, especially under tough conditions, for example, high temperature and aqueous environment [28–34].

In this paper, we utilized H_2pip as ligand and presented a series of Mn(II) complexes with structure dimension from 0D, 2D to 3D, namely, [Mn(Hpip)$_2$(bipy)$_2$(H_2O)$_2$] (**1**), {[Mn(pip^{2-})(bibp)]·DMA}$_n$ (**2**) and [Mn(pip)]$_n$ (**3**), under hydrothermal conditions. Thermal and aqueous stability of complex **2** and **3** were investigated in this context. Furthermore, magnetic property were also studied, which show that compound **2** and **3** both reveal antiferromagnetic behavior. Herein, we report on the synthesis, crystal structures and properties of these complexes.

2. Experimental section

2.1. Materials and general methods

All the chemical reagent of analytical grade were commercially available, and used without further purification. Powder X-ray

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diffraction (PXRD) data under the 2θ range 5–50° were recorded using Cu-Kα radiation ($k = 0.1542$ nm) on a Bruker D8A A25 X-ray diffractometer, with the X-ray tube operated at 40 kV and 40 mA at room temperature. The Elementar Vario Micro Cube analyzer was used to carry out the elemental analyses (C, H, N), and a SHIMADZU DTG-60 thermo analyzer was used to perform the thermogravimetric analyses (TGA) from room temperature to 800 °C under nitrogen protection with a heating rate of 20 °C min^{-1}. Infrared (IR) spectrum of the KBr disks dispersed sample powders were measured on a Thermo Nicolet IR 200 FT-IR spectrometer in the range of 4000–500 cm^{-1}. Magnetic property were performed using a Quantum Design Squid-VSM magnetometer.

2.2. X-ray crystallography

X-ray diffraction data for the single crystal sample of **1**–**3** were collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The SADABS programs was used to apply the empirical absorption correction [35]. Direct methods and full-matrix least-squares methods on F^2 were performed to solve and refine the structure using the SHEXL 97 [36]. All the crystallographic programs were integrated into a system by using the single suite WINGX [37]. All non-hydrogen atoms were refined anisotropically. Geometrically calculations was implemented to locate the hydrogen atoms, and during the structure refinement, positions and thermal parameters of them were fixed as well. The crystallographic data and details of selected bond lengths and angles are summarized in Table 1 and Table S1, respectively.

*2.2.1. Synthesis of [Mn(Hpip)$_2$(bipy)$_2$(H$_2$O)$_2$] (**1**)*

A mixture of $MnCl_2 \cdot 4H_2O$ (0.0395 g, 0.2 mmol), H_2pip (0.0243 g, 0.1 mmol) and 4,4′-Bipyridine (4,4′-bipy) (0.0156 g, 0.1 mmol) were dissolved in distilled water (5 ml) and then heated to 160 °C for 96 h in a 20 ml stainless steel reactor with a Teflon liner. The reaction system was then cooled to room temperature slowly. Colorless block crystals of **1** were obtained with low yield and could hardly be purified.

Table 1
Crystal data and structure refinement parameters for compounds **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{46}H_{36}MnN_6O_{10}$	$C_{35}H_{21}MnN_6O_5$	$C_{13}H_7MnNO_4$
Formula weight	885.73	660.52	296.14
Crystal system	triclinic	triclinic	tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$P4_32_12$
Unit cell dimensions			
a (Å)	8.1130(10)	10.129(6)	8.2020(10)
b (Å)	9.2350(10)	13.293(8)	8.202
c (Å)	14.8010(10)	13.295(8)	33.281(2)
α (°)	83.9990(10)	101.373(11)	90
β (°)	79.4700(10)	101.661(11)	90
γ (°)	68.6890(10)	109.825(10)	90
V (A^3)	1014.84(18)	1579.2(16)	1757
Z	1	2	8
Calculated density (g/cm^3)	1.449	1.389	2.238
F(000)	457	676	1192
θ range for data collection (°)	2.37–27.48	3.26–53.94	2.45–27.47
Goodness-of-fit (GOF) on F^2	1.012	1.062	1.140
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0415$ $wR_2 = 0.0898$	$R_1 = 0.0520$ $wR_2 = 0.1334$	$R_1 = 0.0223$ $wR_2 = 0.0608$
R indices (all data)	$R_1 = 0.0596$ $wR_2 = 0.1004$	$R_1 = 0.0742$ $wR_2 = 0.1486$	$R_1 = 0.0227$ $wR_2 = 0.0610$
Largest difference peak and hole (e A^{-3})	0.302 and −0.332	0.68 and −0.38	0.404 and −0.618

*2.2.2. Synthesis of {[Mn(pip)(bibp)]·DMA}$_n$ (**2**)*

A mixture of $MnCl_2 \cdot 4H_2O$ (0.02 g, 0.1 mmol), H_2pip (0.006 g, 0.025 mmol) and 4,4′-Bis(imidazolyl)biphenyl (bibp) (0.007 g, 0.025 mmol) were placed in a vial, followed by the addition of 1 ml *N*,*N*′-dimethylacetamide (DMA) and 1 ml H_2O. The reaction system was sealed and then heated to 100 °C for 48 h. After cooled

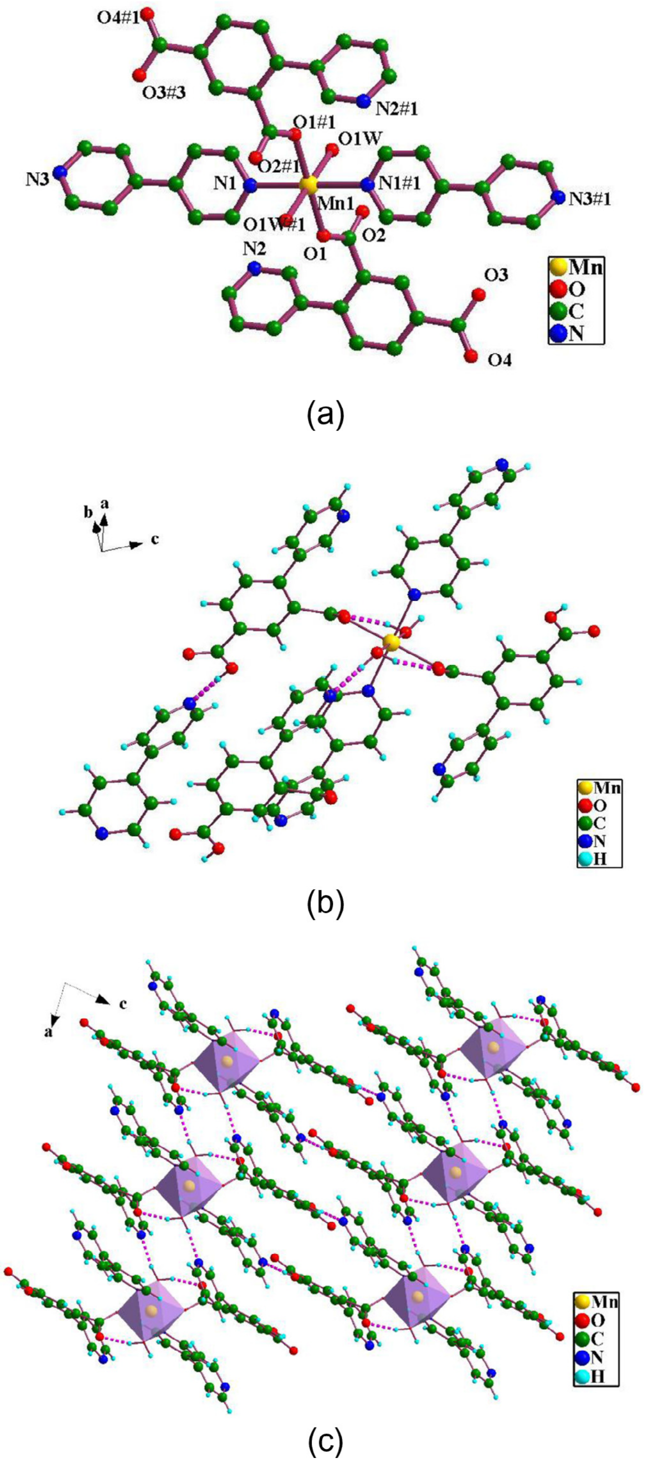

Fig. 1. **(a)** Coordination environment of the Mn (II) in **1**; **(b)** The packing diagram of **1** showing the hydrogen bonding interactions. (pink dashed lines); **(c)** 3D supramolecular structures formed by the hydrogen bonding interactions of **3**. (pink dashed lines) (H atoms omitted for clarity) Symmetry codes: #1 1 − *x*, 1 − *y*, 2 − *z*. (Colour online.)