Xiao-Hong Zhu*, Xiao-Chun Cheng and Yun-Hua Qian

A Mn(II) coordination polymer from a polycarboxylate-containing ligand: synthesis, structural characterization, and properties

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Abstract: The neutral, four-fold protonated pyridine-3,5-dicarbox(3,5-dicarboxylatoanilide) (H_4L) reacts with Mn(II) salts under hydrothermal conditions to yield a new complex: $[Mn_2(L)(H_2O)_2] \cdot H_2O$ (**1**), which has been characterized by single crystal X-ray diffraction, infrared spectroscopy, and elemental and thermogravimetric analyses. Complex **1** exhibits a binodal (4,8)-connected 3D framework with **flu** $(4^{12}.6^{12}.8^4)(4^6)_2$ topology. The magnetic properties of **1** were investigated.

Keywords: coordination polymer; magnetic interaction; Mn(II); structural characterization.

1 Introduction

In recent years, the crystal engineering of coordination polymers has received remarkable attention in view of their beautiful topologies and potential applications [1]. Consequently, a great number of polymers with interesting compositions and properties have been deliberately prepared via self-assembly using a variety of aromatic polycarboxylic ligands and discussed in some comprehensive reviews [2]. However, the self-assembly process is rather complicated and can be influenced by many factors such as the nature of metal ions, the flexibility or rigidity of the ligands, and acidic or basic media for the reaction systems [3]. Therefore, on one hand, it is still a challenge to exactly control the compositions and structures of resultant complexes, and on the other hand, the structures and properties of resultant complexes seem adjustable, which attracted us to do further study to understand the influence of the assembly process [4].

***Corresponding author: Xiao-Hong Zhu,** Jiangsu Provincial Key Laboratory of Palygorskite Science and Applied Technology, Huaiyin Institute of Technology, Huaian 223003, P.R. China, e-mail: hgzhuxh@yeah.net
Xiao-Chun Cheng and Yun-Hua Qian: Jiangsu Provincial Key Laboratory of Palygorskite Science and Applied Technology, Huaiyin Institute of Technology, Huaian 223003, P.R. China

Recently, we have focused our attention on the reactions of metal salts with a polycarboxylic ligand: pyridine-3,5-dicarbox(3,5-dicarboxylatoanilide) (H_4L in its four-fold protonated form) [5]. Our goals are to assembly coordination polymers and explore the influence of intrinsic features of ligands and experimental conditions on the structures of resultant polymers. Our selection is based on the following consideration: carboxylate group could adopt various coordination patterns such as μ_1-η^1:η^0-monodentate, μ_1-η^1:η^1-chelating, and μ_2-η^1:η^1-bridging modes [6]. The four carboxylic acid groups of H_4L could be partially or completely deprotonated by the alkaline reagents to generate L^{4-}, HL^{3-}, H_2L^{2-}, or H_3L^- anions, which could enrich the coordination patterns of H_4L. Given its variable coordination modes, H_4L can be regarded as a reliable candidate as a blocking linker. In this contribution, we report the preparation and characterization of a new coordination polymer $[Mn_2(L)(H_2O)_2] \cdot H_2O$ (**1**). The thermal stability and magnetic properties of **1** were examined.

2 Results and discussion

2.1 Preparation

$MnCl_2 \cdot 4H_2O$ reacts with the neutral, four-fold protonated pyridine-3,5-dicarbox(3,5-dicarboxylatoanilide) (H_4L) in the presence of KOH under the hydrothermal condition at 120°C to produce the complex $[Mn_2(L)(H_2O)_2] \cdot H_2O$ (**1**) which is stable in air.

2.2 Structural description of $[Mn_2(L)(H_2O)_2] \cdot H_2O$ (1)

Complex **1** was obtained, which is a 3D framework based on Mn(II) and the four-fold deprotonated ligand L^{4-}. It crystallizes in the monoclinic space group *C*2/*c* (Table 1). The asymmetric unit of **1** contains one Mn(II), half of L^{4-}, one coordinated water, and 1/2 molecule of lattice water. Mn(II) is pentacoordinated (Fig. 1a) with distorted trigonal bipyramid coordination geometry, by four carboxylate O atoms and one water O atom. The bond distances around

Table 1: Crystal structure data for complex **1**.

$[Mn_2(L)(H_2O)_2]\cdot H_2O$ (1)	
Formula	$C_{23}H_{17}N_3O_{13}Mn$
M_r	653.28
Crystal size, mm³	0.10×0.10×0.10
Crystal system	Monoclinic
Space group	*C*2/*c*
a, Å	17.020(7)
b, Å	16.874(6)
c, Å	7.990(2)
β, deg	96.393(15)
V, Å³	2280.3(13)
Z	4
$D_{calcd.}$, g cm⁻³	1.90
$\mu(MoK_\alpha)$, cm⁻¹	1.2
F(000), *e*	1320
hkl range	±22, ±21, ±10
θ range, deg	3.19–27.48
Refl. measured/unique/R_{int}	10 548/2600/0.0359
Param. refined	196
$R(F)^a/wR(F^2)^b$ (all refls.)	0.0394/0.0895
GoF (F^2)[c]	1.050
$\Delta\rho_{fin}$ (max/min), *e* Å⁻³	0.51/−0.34

[a] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR(F^2)=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w=[\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P=(\mathrm{Max}(F_o^2,0)+2F_c^2)/3$; [c] $\mathrm{GoF}=S=[\Sigma w(F_o^2-F_c^2)^2/(n_{obs}-n_{param})]^{1/2}$.

Mn(II) are from 2.0641(15) to 2.2106(19) Å; the coordination bond angles are in the range of 81.91(7) to 165.01(7)° (Table 2). In complex **1**, the H_4L was wholly deprotonated as a centrosymmetric L^{4-} anion (Scheme 1). Two different carboxylate groups all exhibit μ_2-η^1:η^1-bridging coordination mode, but the pyridyl N atom is free of coordination. So each L^{4-} ligand links eight metal ions as a μ_8-bridge, and each Mn(II) is coordinated by four L^{4-}. This kind of interconnection extends infinitely to form a 3D framework (Fig. 1c). If only half of centrosymmetric L^{4-} is considered, a 2D network can be viewed (Fig. 1b). Topological analysis shows that the architecture of **1** can be simplified as a binodal (4,8)-connected 3D framework with **flu** ($4^{12}.6^{12}.8^4$)(4^6)$_2$ topology (Fig. 1d) [7].

2.3 Thermal stability of complex 1

Thermogravimetric analysis (TGA) was carried out for complex **1**, and the result is shown in Fig. 2. There is a weight loss of 3.0% in the temperature range of 90–120°C which corresponds to the liberation of lattice water (calcd 2.8%). A weight loss of 5.6% from 150 to 220°C is assigned

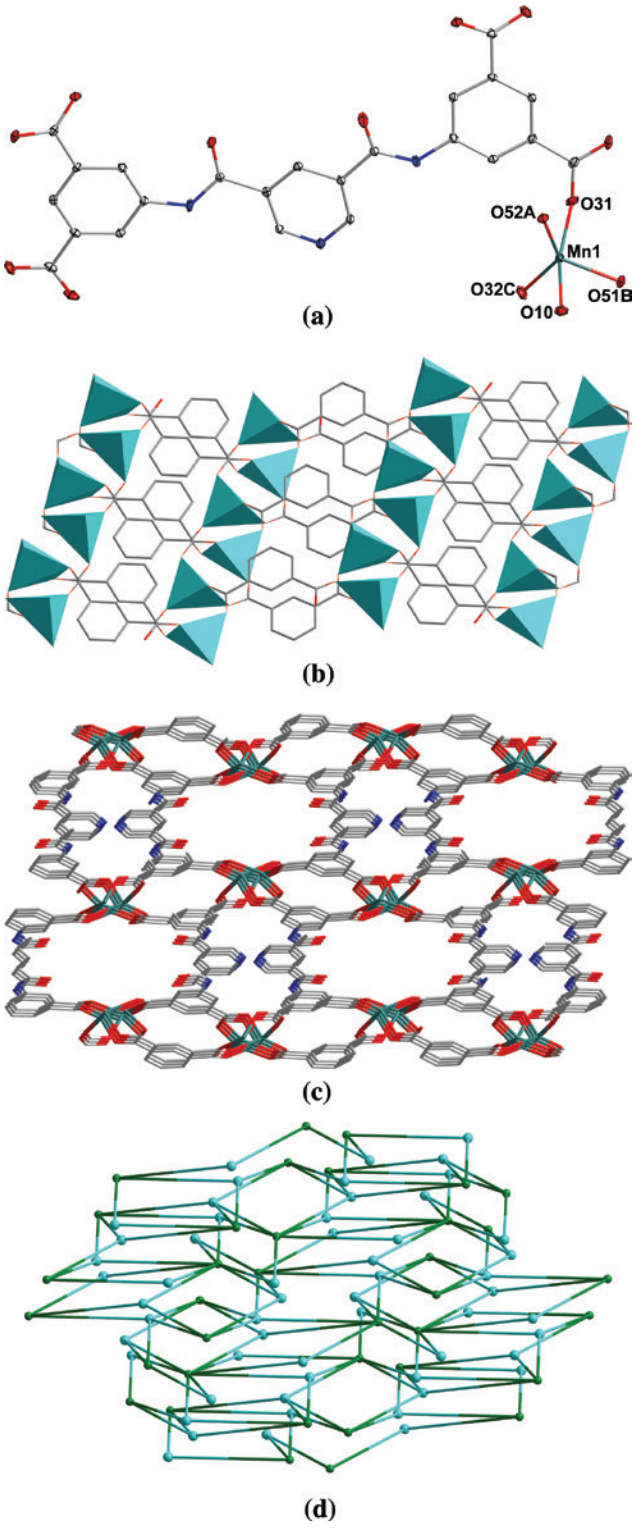
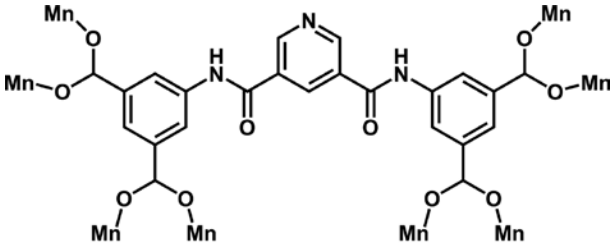


Fig. 1: (a) The coordination environment of Mn(II) in complex **1** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms and lattice water molecules are omitted for clarity. (b) View of the 2D network in **1**. (c) View of the 3D architecture of **1**. (d) Topological view of the 3D framework of **1**.

Table 2: Selected bond lengths (Å) and angles (deg) for complex **1**[a].

$[Mn_2(L)(H_2O)_2]\cdot H_2O$ (1)			
Mn(1)–O(10)	2.211(2)	Mn(1)–O(31)	2.1389(19)
Mn(1)–O(32)#1	2.0781(19)	Mn(1)–O(51)#2	2.0641(18)
Mn(1)–O(52)#3	2.0849(17)		
O(10)–Mn(1)–O(31)	165.00(7)	O(10)–Mn(1)–O(32)#1	94.54(7)
O(10)–Mn(1)–O(51)#2	81.91(7)	O(10)–Mn(1)–O(52)#3	84.91(6)
O(31)–Mn(1)–O(32)#1	99.71(7)	O(31)–Mn(1)–O(51)#2	90.62(6)
O(31)–Mn(1)–O(52)#3	89.07(6)	O(32)#1–Mn(1)–O(51)#2	101.58(7)
O(32)#1–Mn(1)–O(52)#3	131.64(6)	O(51)#2–Mn(1)–O(52)#3	125.97(6)

[a]Symmetry transformations used to generate equivalent atoms: for **1**: #1 x, $1-y$, $1/2+z$; #2 $1/2-x$, $1/2+y$, $1/2-z$; #3 $1/2-x$, $1/2-y$, $1-z$.



Scheme 1

Scheme 1: Coordination modes of H_4L appearing in complex **1**.

to the release of coordinated water (calcd 5.5%), and the decomposition of the residue can be observed at 420°C.

2.4 Magnetic properties of complex 1

The Mn(II) cations in **1** are bridged by carboxylate, which may mediate magnetic interactions [8]. Thus, the temperature dependence of the magnetic susceptibility of **1** was investigated from 300 to 1.8 K with an applied magnetic field of 2000 Oe. The χ_M, χ_M^{-1}, and $\chi_M T$ vs. T curves for **1** are shown in Fig. 3.

The value of $\chi_M T$ at 300 K is 7.66 emu K mol^{-1} which is larger than the value expected for a magnetically isolated Mn(II) cation (4.38 emu K mol^{-1}, $g=2.0$) due to spin–orbital coupling, indicating a significant orbital contribution [8]. The temperature dependence of χ_M^{-1} above 50 K obeys the Curie–Weiss equation of $\chi_M^{-1}=(T-\theta)/C$ with the constants $C=8.27$ cm^3 mol^{-1} K and $\theta=-18.4$ K.

The negative value of θ and the shape of the $\chi_M T$ vs. T curve suggest that there may exist antiferromagnetic interactions between the neighboring Mn(II) centers [9]. In order to estimate the strength of the magnetic interactions in **1**, the following equation was used [10]:

$$\chi_M T = A\exp(-E_1/kT) + B\exp(-E_2/kT)$$

Here, $A+B$ equals the Curie constant (C), and E_1, E_2 represent the 'activation energies' corresponding to the spin–orbit coupling and the magnetic exchange interaction,

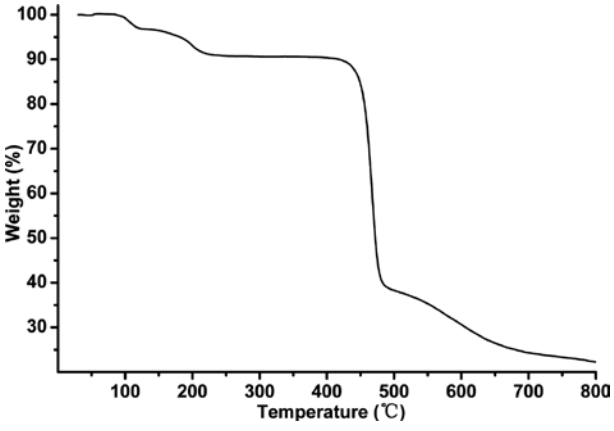


Fig. 2: TGA curve of complex **1**.

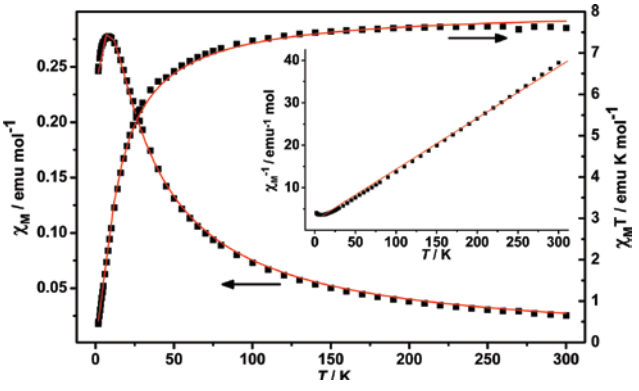


Fig. 3: Temperature dependence of magnetic susceptibility χ_M, χ_M^{-1}, and $\chi_M T$ for **1**. The solid lines represent the fitted curve.

respectively. The obtained values of $A+B=8.34$ cm^3 mol^{-1} K and $E_1/k=10.6$ K agree with those given in a previous report [10]. The value of $-E_2/k=-1.68$ K corresponding to $J=-3.76$ K further proves that antiferromagnetic interactions exist between neighboring Mn(II) ions in **1** [11].

3 Experimental section

All commercially available chemicals were of reagent grade and used as received without further purification. The H_4L ligand was synthesized via the experimental procedure reported in the literature [5]. Elemental analysis of C, H, and N was taken on a Perkin-Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. TGA was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10°C min^{-1}. The magnetic measurement in the temperature range of 1.8–300 K was carried out on a Quantum Design MPMS7 SQUID magnetometer in a field of 2 kOe (1 kOe $=7.96\times10^4$ A m^{-1}). Diamagnetic corrections were made with Pascal's constants.

3.1 Preparation of $[Mn_2(L)(H_2O)_2]\cdot H_2O$ (1)

The reaction mixture of H_4L (0.05 mmol, 24.7 mg), $MnCl_2\cdot4H_2O$ (0.10 mmol, 14.3 mg), and KOH (11.2 mg, 0.2 mmol) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless steel container and heated at 120°C for 3 days. After cooling to room temperature, colorless block crystals of **1** were collected by filtration and washed with water and ethanol several times (yield 50% based on H_4L). – $C_{23}H_{17}N_3O_{13}Mn_2$ (653.28): calcd. C 42.29, H 2.62, N 6.43; found C 42.50, H 2.42, N 6.26%. – IR (KBr pellet, cm^{-1}): $\nu=3459$ (m), 1621 (s), 1570 (s), 1468 (s), 1440 (s), 1417 (s), 1359 (s), 1238 (m), 1139 (m), 1061 (s), 879 (m), 762 (s), 733 (m), 647 (m), 586 (m).

3.2 X-ray structure determination

The crystallographic data collection for complex **1** was carried out on a Bruker Smart ApexII CCD area-detector diffractometer using graphite-monochromatized MoK_α radiation ($\lambda=0.71073$ Å) at $T=293(2)$ K. The diffraction data were integrated by using the program SAINT [12], which was also used for the intensity corrections for Lorentz and polarization effects. Semi-empirical absorption corrections were applied using the program SADABS [13]. The structure of **1** was solved by Direct Methods, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares techniques using the SHELXS/L-97 crystallographic software package [14–18]. In **1**, all hydrogen atoms at C atoms were generated geometrically, while the ones of O1, O10, and N1 were found at reasonable positions in the difference Fourier maps and located there. The bond distance of N(1)–H(1) was restricted to 0.87 ± 0.01 Å for a more reasonable length. The details of crystal parameters, data collection, and the graphite refinement are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC 1501754 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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