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Synthesis, Strucure, and Magnetic Property of a 3D Mn(II) Coordination Polymer Based on 2,3',5,5'-Bophenyl Tetracarboxylic Acid[1]

X. N. Zhang and Z. B. Han*

College of Chemistry, Liaoning University, Shenyang, 110036 P.R. China

**e-mail: ceshzb@lnu.edu.cn*

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Abstract—A new coordination polymer $Mn_2(L)(DMF)_2(H_2O)_2$ (**I**), H_4L = 2,3',5,5'-biphenyl tetracarboxylic acid has been synthesized under hydrothermal conditions and characterized by elemental analysis, IR, TG and single-crystal X-ray diffraction. The X-ray diffraction analysis shows that **I** ($C_{22}H_{20}Mn_2N_2O_{12}$) crystallizes in the monoclinic crystal system space group $P2_1$. The magnetic studies of I showed that there exist antiferromagnetic interactions between the Mn(II) centres. The unit cell parameters for **I**: a = 9.6271(13), b = 13.1172(17), c = 10.5726(14) Å, β = 110.084(2)°, V = 1253.9(3) Å^3, Z = 2.

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INTRODUCTION

Over the past decade, metal-organic frameworks (MOFs) have attracted much attention, not only for their compositional and structural diversities, but also for their potential applications in the areas of catalysis [1–3], luminescence [4–7], gas adsorption and separation [8–10], ion exchanging [11, 12], magnetism [13–16] and so on. In the design and construction of these frameworks organic ligands play crucial roles as even small changes in flexibility, length, or symmetry of the ligands can result in a remarkable diversity of architectures and functions [17–19]. Recently, a large number of organic ligands as potential linkers, polynuclear coordination polymers consisting carboxylate ligands have witnessed the most important development [20]. To the best of our knowledge, complexes based on 2,3',5,5'-biphenyl tetracarboxylic ligand have been rarely reported [21]. Therefore, we select 2,3',5,5'-biphenyl tetracarboxylic acid (H_4L) considering that its four carboxyl groups can provide versatile binding fashions. In this paper, we report on the synthesis, crystal structure and magnetic properties of $Mn_2(L)(DMF)_2(H_2O)_2$ (**I**), constructed from L^{4-} ligands with Mn(II), which exists antiferromagnetic interactions between the Mn(II) centers.

EXPERIMENTAL

Materials and methods. All solvents and reagents employed were commercially available and used without further purification. The C, H, and N microanalyses were carried out on a PerkinElmer 240 elemental analyzer. Thermogravimetric analyses (TGA) were taken with PerkinElmer Pyrisl (30–900°C, 10°C/min, flowing N_2(g)). X-ray powder diffraction was registered with a Bruker AXS D8 advanced automated diffractometer with CuK_α radiation. Infrared spectra were recorded on the powder samples of a crystal embedded in KBr pellets from 400 to 4000 nm at a speed of 100 nm/min. The magnetic data were collected on a Quantum Design MPMS SQUID-XL-5 magnetometer using the crushed single-crystal samples. Magnetic data were corrected for the diamagnetic contribution calculated from Pascal constants [22] and a background of the sample holder.

Solvothermal synthesis of I. $Mn(NO_3)_2 \cdot 6H_2O$ (0.26 mmol) was added to the DMF–CH_3CH_2OH–H_2O (3 : 3 : 2; 4 mL) solution of H_4L (15 mg, 0.45 mmol), and the mixture was stirred for ~20 min in air. Then it was heated at 75°C for 2 days, followed by slow cooling (5°C h^{-1}). The resulting light yellow crystals were washed with distilled water and dried in air (the yield was ~60%).

For $C_{22}H_{20}N_2O_{12}Mn_2$

anal. calcd., %:	C, 36.01;	H, 3.27;	N, 3.82.
Found, %:	C, 36.09;	H, 3.20;	N, 4.80.

IR spectrum (KBr; ν, cm^{-1}): 3388 m, 1656 s, 1627 m, 1582 m, 1495 s, 1385 s, 775 m.

X-ray crystal determination. Crystallographic data of **I** was collected at room temperature (293(2) K) with a Bruker P4 diffractometer with MoK_α radiation (λ = 0.71073 Å) and graphite monochromator using the ω-scan mode. The structure was solved by direct

[1] The article is published in the original.

Table 1. Crystallographic data and structural refinement summary for **I**

Parameter	Value
Formula weight	614.28
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
α, Å	9.6271(13)
b, Å	13.1172(17)
c, Å	10.5726(14)
β, deg	110.084(2)
V, Å^3	1253.9(3)
Z	2
μ, mm^{-1}	1.074
F(000)	624
θ Range for data collection, deg	2.2–26.00
Reflections collected	7262
Max, min transmission	0.7988, 0.6997
Data/restraints/parameters	4672/1/344
Final *R* indices ($I > 2\sigma,(I)$)*	$R_1 = 0.0492$, $wR_2 = 0.1260$
R indices (all data)	$R_1 = 0.0573$, $wR_2 = 0.1310$
Largest diff. peak and hole, *e* Å^{-3}	0.964, –0.649
Reflections collected	7262

* $R_1 = \Sigma\|\|F_o| - |F_c\|\|/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

methods and refined on F^2 by full-matrix least-squares using SHELXTL [23]. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 1023460; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

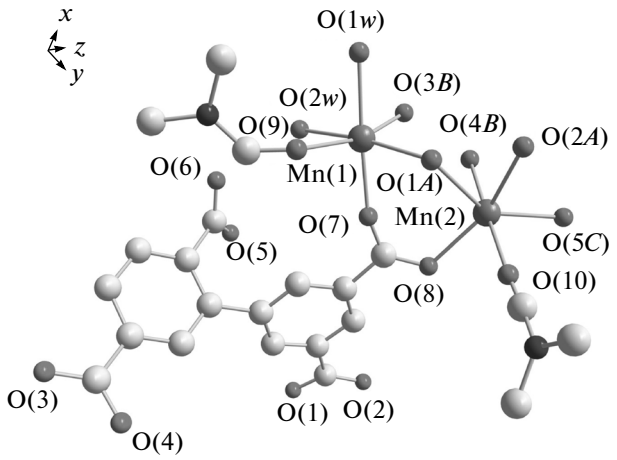


Fig. 1. Coordination environment of the Mn(II) centres in **I** (H atoms are omitted for clarity). Symmetry mode: (*A*) $x - 1, y, z$; (*B*) $x - 1, y, z - 1$; (*C*) $-x, 0.5 + y, -z + 1$.

RESULTS AND DISCUSSION

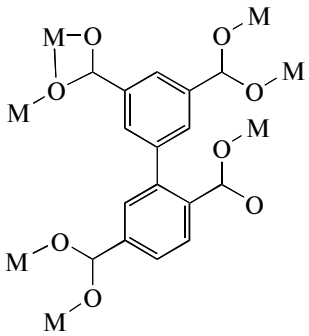
The asymmetric unit of **I** contains two crystallographically unique Mn(II) ions, one L ligand, two coordinated DMF molecules and two aqua ligands. As shown in Fig. 1, the Mn(1) atom is six-coordinate with three carboxylate oxygen atoms from three individual L ligands (Mn(1)–O(1) 2.175(4), Mn(1)–O(3) 2.135(5) Å, Mn(1)–O(7) 2.106(5) Å), one oxygen atoms from one coordinated DMF molecule (Mn(1)–O(9) 2.227(4) Å), and two aqua ligands (Mn(1)–O(1*w*) 2.185(5) Å, Mn(1)–O(2*w*) 2.208(4) Å). Like Mn(1), Mn(2) atom is also six-coordinate with five carboxylate oxygen atoms from four individual L ligands (Mn(2)–O(1) 2.513(4) Å, Mn(2)–O(2) 2.322(4) Å, Mn(2)–O(4) 2.090(4), Mn(2)–O(5) 2.162(4), Mn(2)–O(8) 2.209(4) Å) and one oxygen atom from one coordinated DMF molecule (Mn(2)–O(10) 2.161(6) Å). Mn(1) is linked to Mn(2) via two μ_2-η^2:η^1 bidentate carboxylate groups and one μ_2-η^1:η^1 carboxylate group to form a dinuclear Mn cluster. The Mn clusters are bridged by L ligands to form a three-dimensional (3D) framework. It is noted

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	*d*, Å	Bond	*d*, Å
Mn(1)–O(7)$^{\#1}$	2.106(5)	Mn(2)–O(4)$^{\#2}$	2.090(4)
Mn(1)–O(3)$^{\#2}$	2.135(5)	Mn(2)–O(10)	2.161(6)
Mn(1)–O(1)	2.175(4)	Mn(2)–O(5)$^{\#3}$	2.162(4)
Mn(1)–O(1*w*)	2.185(5)	Mn(2)–O(8)$^{\#1}$	2.209(4)
Mn(1)–O(2*w*)	2.208(4)	Mn(2)–O(2)	2.322(4)
Mn(1)–O(9)	2.227(4)	Mn(2)–O(1)	2.513(4)
Angle	ω, deg	Angle	ω, deg
O(7)$^{\#1}$Mn(1)O(3)$^{\#2}$	96.6(2)	O(4)$^{\#2}$Mn(2)O(10)	178.6(2)
O(7)$^{\#1}$Mn(1)O(1)	79.4(2)	O(4)$^{\#2}$Mn(2)O(5)$^{\#3}$	89.64(18)
O(3)$^{\#2}$Mn(1)O(1)	95.51(17)	O(10)Mn(2)O(5)$^{\#3}$	89.6(2)
O(7)$^{\#1}$Mn(1)O(1*w*)	176.7(2)	O(4)$^{\#2}$Mn(2)O(8)$^{\#1}$	96.26(18)
O(3)$^{\#2}$Mn(1)O(1*w*)	82.8(2)	O(10)Mn(2)O(8)$^{\#1}$	85.1(2)
O(1)Mn(1)(1*w*)	97.46(19)	O(5)$^{\#3}$Mn(2)O(8)$^{\#1}$	119.80(18)
O(7)$^{\#1}$Mn(1)O(2*w*)	93.0(2)	O(4)$^{\#2}$Mn(2)O(2)	91.36(19)
O(3)$^{\#2}$Mn(1)O(2*w*)	84.18(19)	O(10)Mn(2)O(2)	87.4(2)
O(1)Mn(1)O(2*w*)	172.29(18)	O(5)$^{\#3}$Mn(2)O(2)	86.53(17)
O(1*w*)Mn(1)O(2*w*)	90.2(2)	O(8)$^{\#1}$Mn(2)O(2)	152.49(16)
O(7)$^{\#1}$Mn(1)O(9)	95.2(2)	O(4)$^{\#2}$Mn(2)O(1)	88.39(15)
O(3)$^{\#2}$Mn(1)O(9)	164.25(19)	O(10)Mn(2)O(1)	91.44(19)
O(1)Mn(1)O(9)	96.90(17)	O(5)$^{\#3}$Mn(2)O(1)	140.71(16)
O(1*w*)Mn(1)O(9)	86.0(2)	O(8)$^{\#1}$Mn(2)O(1)	99.41(14)
O(2*w*)Mn(1)O(9)	84.82(18)	O(2)Mn(2)O(1)	54.31(13)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x-1, y, z$; $^{\#2}$ $x-1, y, z-1$; $^{\#3}$ $-x, y+1/2, -z+1$.

that four carboxylate groups in the L ligand exhibit three kinds of connection modes: monodentate, bidentate bridging and chelating/bridging mode and all the carboxylate groups are deprotonated



It is worth mentioning that regardless of the coordinated DMF molecules, it showed 1D channels with the size of ~11.4 × 9.7 Å^2 along the *y* axis (Fig. 2). With omitting the coordinated DMF molecules, PLATON analysis [24] revealed that the 3D framework was composed of voids of 562.2 Å^3, which represent 44.1% per unit cell volume.

The IR spectrum of **I** shows characteristic bands of carboxyl groups at 1656, 1627 cm^{-1} for the antisymmetric stretching and at 1582, 1495 cm^{-1} for symmetric stretching. The separations (Δ) between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ indicate the presence of monoatomic (221 cm^{-1}), bidentate bridging (132 cm^{-1}) and chelating (74 cm^{-1}) coordination modes in **I** [25]. The absence of strong peaks around 1700 cm^{-1} in **I** indicates that all carboxylic groups are deprotonated [26], which is consistent with the results of the valence sum calculations. According to near 3388 cm^{-1}, strong and broad absorption peaks are attributed to the O–H vibration absorption of water molecules.

The temperature-dependent magnetic susceptibilities of complex **I** were investigated at a temperature range of 2–300 K, under an applied field of 1000 G, in the form $\chi_M T$ vs. T and χ_M vs. T, where χ_M is the molar magnetic susceptibility (Fig. 3). For complex **I**, the $\chi_M T$ value per Mn(2) unit at 300 K is 8.21 cm^3 mol^{-1} K, which is lower than the spin-only value 8.75 cm^3 mol^{-1} K expected for two magnetically isolated Mn^{2+} ions ($S = 5/2$, $g = 2.0$) [27]. By decreasing the temperature, the $\chi_M T$ gradually decreases from 300 to ~120 K, then a little more steeply, reaching

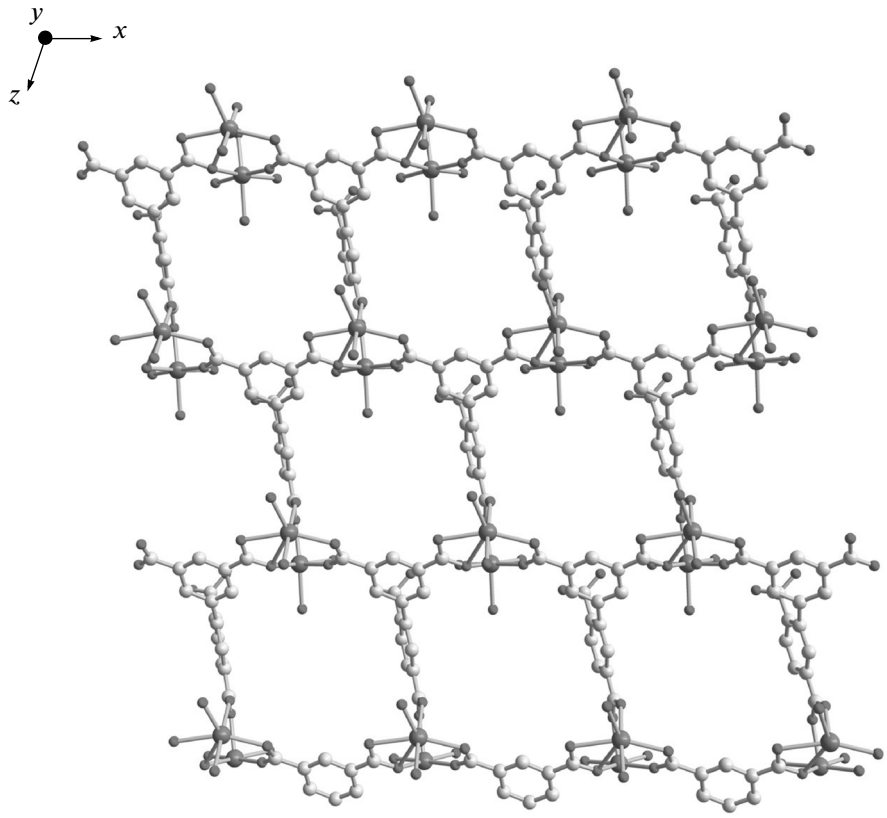


Fig. 2. 3D single network of **I** along the *y* axis with removing coordinated DMF molecule.

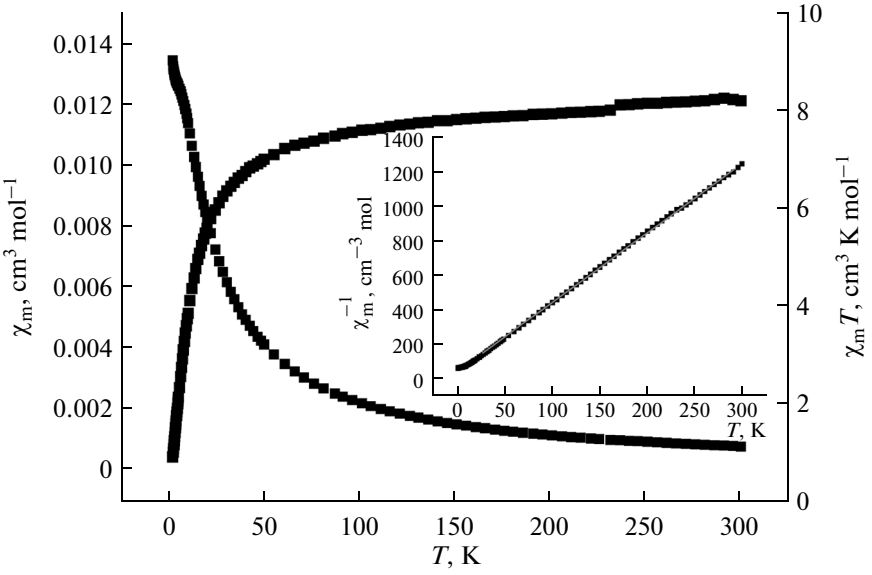


Fig. 3. Temperature dependence of $\chi_M T$ and χ_M under an applied field of 1000 G for **I**.

0.91 cm^3 mol^{-1} K at 2.0 K, suggesting a dominant antiferromagnetic interaction between Mn(II) centres [28]. The inverse susceptibility plot as a function of temperature is linear above 100 K, following the Curie–Weiss law with a Weiss constant, $\theta = -12.73$ K, and a Curie constant, $C = 0.25$ cm^3 K mol^{-1}, the negative Weiss constant indicating that there exists predominantly antiferromagnetic interaction between two adjacent Mn(II) centres.

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