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ORIGINAL PAPER

Synthesis, Crystal Structure, Magnetic Properties of a Manganese(II) Coordination Polymer with Double-Helix Chains

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Abstract A new heterocyclic carboxylate ligand, 5-(4′-pyridyl)-3-methyl-benzoic acid (Hpmba), was synthesized to construct a Mn(II) coordination polymer, namely $[Mn(pmba)_2]_n$ (**1**). Complex **1** crystallizes in monoclinic space group *C*2/c, with $a = 17.44(2)$, $b = 17.040(12)$, $c = 8.680(15)$ Å, $\beta = 111.258(13)$, $V = 2404(5)$ Å^3, and $Z = 4$. Single-crystal X-ray diffraction studies show that complex **1** has a 3D metal-organic supramolecular framework consisting of double helical chains. Magnetic studies for complex **1** show antiferromagnetic coupling between the nearest Mn(II) ions, with $g = 2.11$ and $J = -10.1$ cm^{-1}.

Keywords Manganese (III) coordination polymer · 5-(4′-Pyridyl)-3-methyl-benzoic acid · Double helical chains · Magnetic property

Introduction

Recently, the design and synthesis of transition metal coordination polymers with helical structures have received enormous attention not only for their intriguing structures but also for their potential applications in molecular recognition, nonlinear optical materials, asymmetric catalysis, enantiomorph separation [1–6]. The construction of helical structures is the result of a combination of various forces, including not only strong interactions (for example metal–ligand coordination bonds) [7, 8] but also weaker interactions such as hydrogen bonds [9, 10] and π–π stacking interactions [11, 12]. We have made efforts for the design and construction of helical structures by coordination interactions between the ligand and the metal. Up to now, we have synthesized a series of such complexes with single-, double-, and multi-stranded helices [13–16]. Herein, we report the synthesis, crystal structure, magnetic properties of a Mn(II) compound with double helix chains.

Experimental

Materials and Physical Measurements

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TG) data were collected on a Netzsch TG-209 instrument with a heating rate of 10 °C/min. Magnetic susceptibility data were collected in the 2–300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

Synthesis of 5-(4′-Pyridyl)-3-Methyl-Benzoic Acid (Hpmba)

Following the protocol of Chia and Lautens [17], a mixture of 4-pyridylboronic acid (0.068 g, 0.55 mmol),

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5-Bromo-3-methylbenzoic acid (0.11 g, 0.5 mmol), K_2CO_3 (0.21 g, 1.5 mmol), $Pd(OAc)_2$ (0.056 g, 0.025 mmol) and 50 mL C_2H_5OH was stirred and refluxed for 8 h. Then as much alcohol as possible was distilled off. The residue was partitioned between water and acetic ether (40 mL, v:v = 1:1). Then the water layer was collected. Some of white precipitate was obtained during 0.5 M hydrochloric acid was added to the water layer until pH = 6.0, and collected by filtration, washed with water, and dried in oven at 105 °C for 6 h. Yield 0.075 g, 70%. Found for $C_{13}H_{11}NO_2$ (213.23 g mol^{-1}): C, 72.86; H, 5.57; N, 6.28. Anal. Calcd: C, 73.22; H, 5.20; N, 6.57. IR (KBr, cm^{-1}): v (CO_2) 1697. ^1H NMR (400 MHz, DMSO-d_6): δ 2.466 (s, 3H), δ 7.743 (s, 1H), δ 7.813 (d, $J = 9.8$ Hz, 2H), δ 7.872 (s, 1H), δ 8.485 (s, 1H), δ 8.700 (d, $J = 11.6$ Hz, 2H), δ 13.415 (bs, 1H).

Table 1 Crystallographic data and refinement summary for complex **1**

Formula	$C_{26}H_{20}N_2MnO_4$
Mr	479.38
Crystal system	Monoclinic
Space group	*C*2/c
a (Å)	17.44(2)
b (Å)	17.040(12)
c (Å)	8.680(15)
β (°)	111.258(13)
V ($Å^3$)	2404(5)
Z	4
T (K)	293(2)
D_{calc} (g cm^{-3})	1.325
Crystal size (mm^3)	0.28 × 0.26 × 0.24
F(000)	988
μ (Mo-Kα)/mm^{-1}	0.582
θ (°)	2.39–25.20
Reflections collected	8457
*R*int	0.0931
Independent reflections($I \geq 2\sigma(I)$)	2174
Max. and min. transmission	0.8728/0.8539
Limiting indices	$-19 \leq h \leq 20$, $-20 \leq k \leq 20$, $-10 \leq l \leq 10$
Parameters	151
$\Delta(\rho)$(e·$Å^{-3}$)	0.276, −0.304
Goodness-of-fit	1.025
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0573$, w$R_2 = 0.1007$
R indices (all data)	$R_1 = 0.0963$, w$R_2 = 0.1149$
CCDC No.	824906

Synthesis of $[Mn(pmba)_2]_n$ (**1**)

A mixture of $MnSO_4·2H_2O$ (0.034 g, 0.2 mmol), Hpmba (0.085 g, 0.4 mmol), NaOH (0.016 g, 0.4 mmol) and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Colourless block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield 0.039 g, 80% (based on Mn). Found for $C_{26}H_{20}N_2MnO_4$ (479.38 g mol^{-1}): C, 65.57; H, 3.98; N, 5.43. Anal. Calcd: C, 65.14; H, 4.20; N, 5.84. IR (KBr, cm^{-1}): $v_{as}(CO_2)$ 1620 and 1561, $v_s(CO_2)$ 1447 and 1387.

X-ray Crystallography

Single-crystal data for compound **1** were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved using direct method, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations during the final state of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 system [18]. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **1**

Mn(1)–O(1)	2.112(3)	Mn(1)–O(1)#1	2.112(3)	Mn(1)–O(2)#2	2.124(3)
Mn(1)–O(2)#3	2.124(3)	Mn(1)–N(1)#4	2.314(3)	Mn(1)–N(1)#5	2.314(3)
O(1)#1–Mn(1)–O(1)	94.25(16)	O(1)#1–Mn(1)–O(2)#2	86.14(13)	O(1)–Mn(1)–O(2)#2	102.21(13)
O(1)#1–Mn(1)–O(2)#3	102.21(13)	O(1)–Mn(1)–O(2)#3	86.14(13)	O(2)#2–Mn(1)–O(2)#3	167.84(15)
O(1)#1–Mn(1)–N(1)#4	89.24(13)	O(1)–Mn(1)–N(1)#4	169.92(11)	O(2)#2–Mn(1)–N(1)#4	87.45(13)
O(2)#3–Mn(1)–N(1)#4	83.88(13)	O(1)#1–Mn(1)–N(1)#5	169.92(11)	O(1)–Mn(1)–N(1)#5	89.24(13)
O(2)#2–Mn(1)–N(1)#5	83.88(13)	O(2)#3–Mn(1)–N(1)#5	87.45(13)	N(1)#4–Mn(1)–N(1)#5	88.92(18)

Symmetry codes: #1: $-x, y, -z + 1/2$; #2: $-x, -y, -z + 1$; #3: $x, -y, z - 1/2$; #4: $x - 1/2, y - 1/2, z - 1$; #5: $-x + 1/2, y - 1/2, -z + 3/2$

Results and Discussion

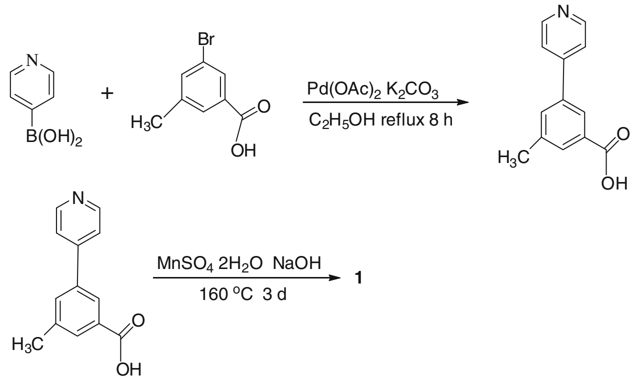
Syntheses

Hpmba was synthesized by the Suzuki reaction and compound **1** was obtained by hydrothermal reaction (Scheme 1). The reaction route is as follows:

Description of Crystal Structure

Crystallographic analysis reveals that complex **1** crystallizes in the monoclinic space group *C*2/c. As shown in Fig. 1, the Mn(II) atom is six-coordinated by four carboxylate atoms and two N atoms from six different pmba ligands, forming a distorted octahedral geometry with three O atoms and one N atom from four individual pmba ligands occupy the equatorial positions, one O atom and one N atom from two different pmba ligand occupy the axial positions. The Mn–O distances range from 2.112(3) to 2.124(4) Å, the Mn–N distances are 2.314(4) Å, which are in good agreement with those observed in other Mn(II) complexes [13, 19, 20]. The pmba ligand adopts the coordination mode of μ_3-tridentate and its carboxylic group adopts μ_2–η^1–η^1 bridging mode in syn–syn conformation, as shown in Scheme 2. The phenyl and pyridyl rings are not coplane with the dihedral angle of ca. 42.71°.

The carboxylate of the pmba ligand bridges alternately two Mn(II) ions in syn–syn coordination mode to form infinite right-handed or left-handed helical C–O–Mn chains (Fig. 2). The Mn···Mn separation in the chain is 4.848(4) Å. The two types of helical chains are interconnected to each other through the Mn(II) centers to produce double-helix chains. The chains are further extended into a



Scheme 1 The synthetic routes for the ligand and compound **1**

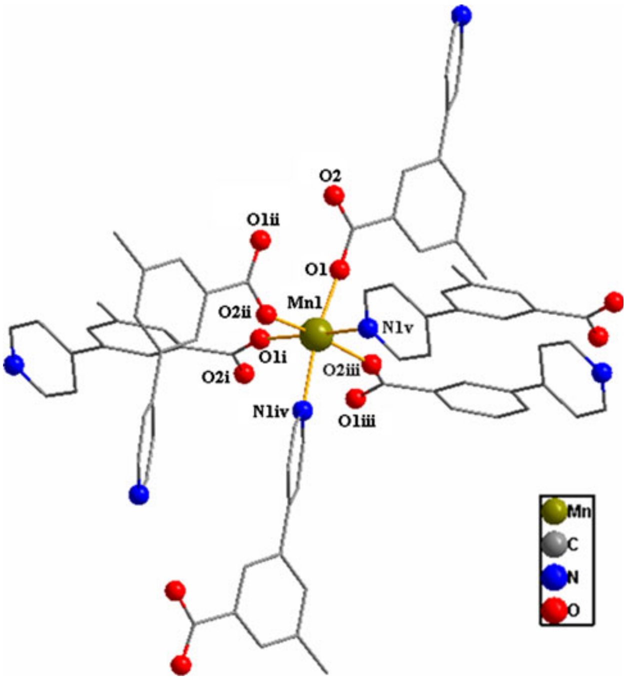
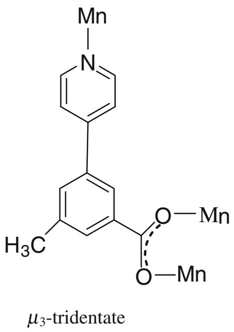


Fig. 1 The coordination environment of Mn^{2+} in **1**. (H atoms were omitted for clarity). Symmetry code: *i* −*x*, *y*, −*z* + 1/2; *ii* −*x*, −*y*, −*z* + 1; *iii x*, −*y*, *z* − 1/2; *iv x* − 1/2, *y* − 1/2, *z* − 1; *v* −*x* + 1/2, *y* − 1/2, −*z* + 3/2



Scheme 2 The coordination mode of the pmba ligand in complex **1**

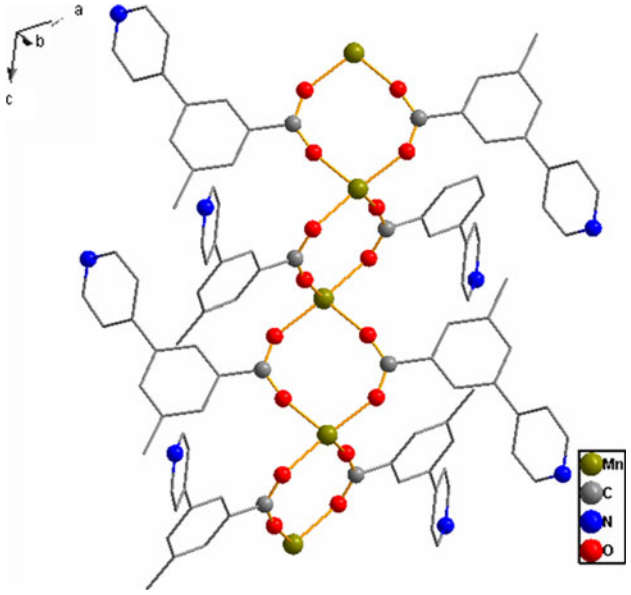


Fig. 2 View of double-helix chains of compound **1**

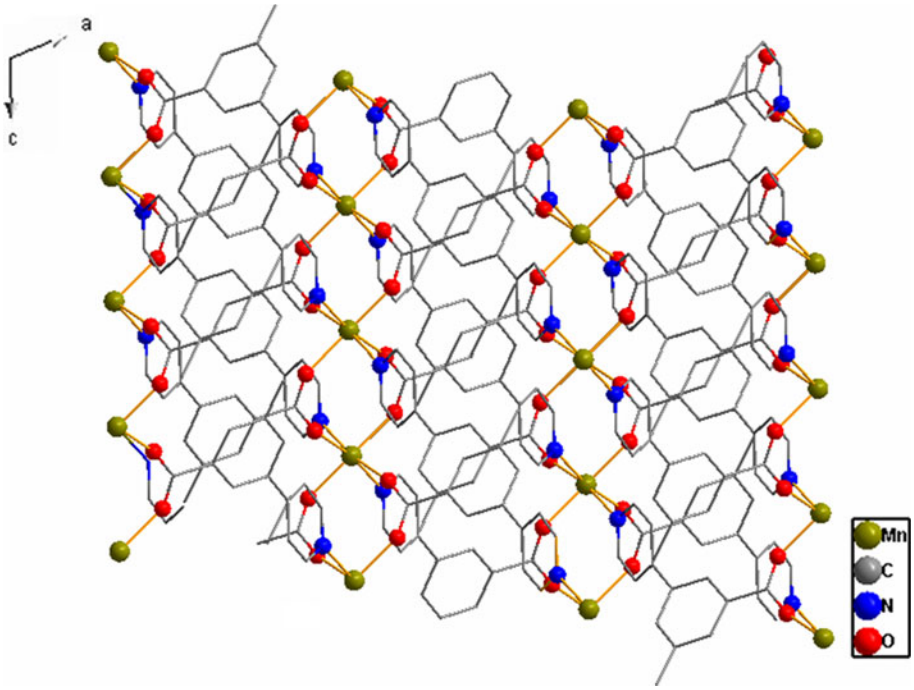


Fig. 3 View of 2D sheet of compound **1** through the coordination interaction of pmba ligands

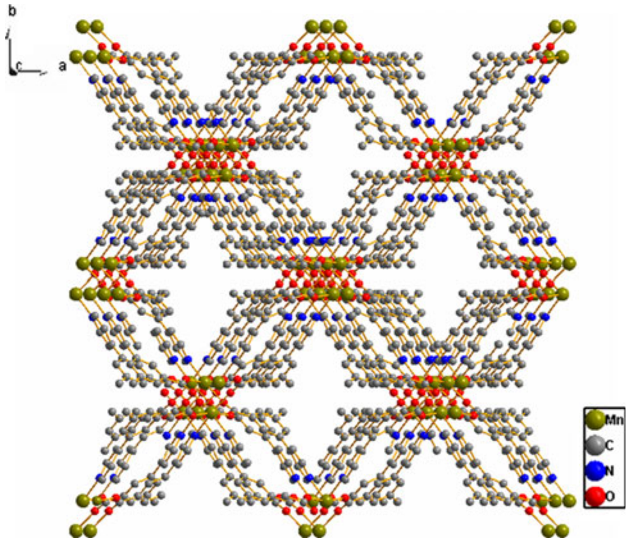


Fig. 4 View of the 3D framework of compound **1** along *c* axis (H atoms were omitted for clarity)

3D metal-organic supramolecular framework by the coordination interaction of the pmba ligands (Figs. 3, 4).

Thermal Analysis and Magnetic Properties

In order to examine the thermal stability of the network, thermal gravimertric analysis (TG) was conducted on crystalline samples of compound **1** between 20 and 800 °C. As shown in Fig. 5, complex **1** is stable up to 425 °C, but decomposes above 425 °C, which corresponds to decomposition of the ligand.

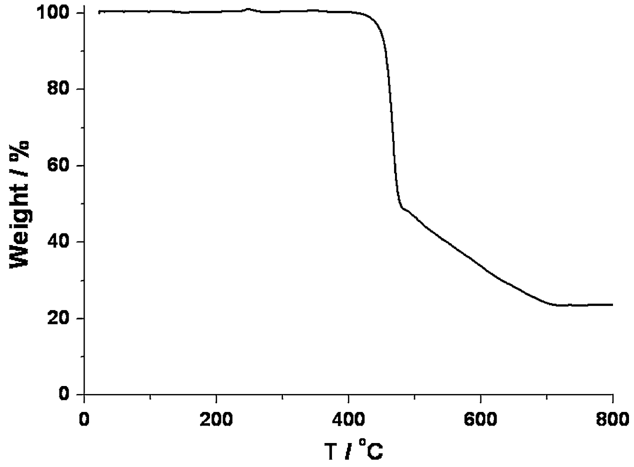


Fig. 5 The TG curve for compound **1**

The temperature-dependent magnetic properties of **1** are shown in Fig. 6 in the form of $\chi_M T$ versus T curve. The $\chi_M T$ value of 4.58 $cm^3 mol^{-1}$ K (6.05 μ_B) at room temperature is close to the value of 4.38 $cm^3 mol^{-1}$ K (5.92 μ_B) expected for magnetically isolated high-spin Mn(II) ($S_{Mn} = 5/2$, $g = 2.0$). The $\chi_M T$ values steadily decreases with decreasing temperature to reach minimum values of 3.86 $cm^3 mol^{-1}$ K at 46.9 K. Between 46.9 and 300 K, the magnetic susceptibilities can be fitted to the Curie–Weiss law, $\chi_M = C_M/(T - \theta)$, with $C_M = 4.77$ $cm^3 mol^{-1}$, $\theta = -14.6$ K. These results indicate an antiferromagnetic interactions between the nearest Mn(II). Upon further cooling, the $\chi_M T$ values increase up to maximum of 4.56 $cm^3 mol^{-1}$ K at $T_N = 37.8$ K, and then decrease with

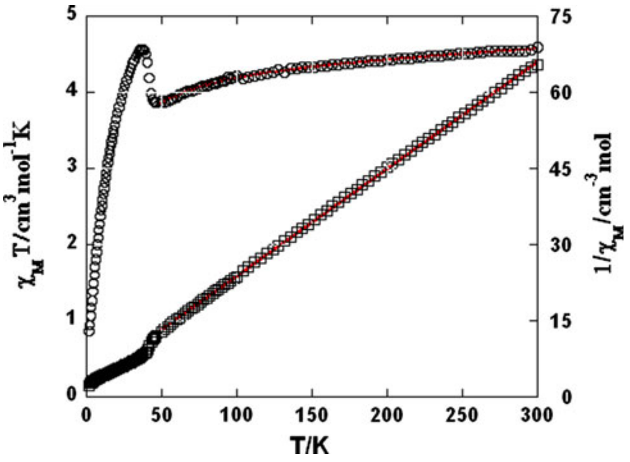


Fig. 6 Temperature dependence of $\chi_M T$ (*open circle*) and $1/\chi_M$ (*open square*) versus T for complex **1**. The *black straight line* shows the Curie–Weiss fitting and the *black curve* shows the best-fit curve, respectively

decreasing temperature. This effect might be related to a spin canted antiferromagnetic behavior with a weak ferromagnetic ordering taking place below the Neel temperature [21]. Since the Mn(II) double-helix chains in **1** are well separated by the long linkers of pmba bridges, the antiferromagnetic behavior could arise from intrachain magnetic interactions of the adjacent Mn(II) centers. According to the chain topology, magnetic exchange pathway consists of two syn–syn carboxylate bridges.

We tried to fit the magnetic data of **1** using the following expression for a 1D Mn(II) chain [22]:

$$\chi_{\mathrm{chain}} = (Ng^2\beta^2/kT)\left[A + Bx^2\right]\left[1 + Cx + Dx^3\right]^{-1}$$

with $A = 2.9167$, $B = 208.04$, $C = 15.543$, $D = 2707.2$ and $x = |J|/kT$

Using this rough model, the susceptibilities for **1** above 46.9 K were simulated, leading to $J = -10.1\ \mathrm{cm}^{-1}$, $g = 2.11$, and the agreement factor $R = 3.86 \times 10^{-6}$.

Conclusion

A new Mn(II) coordination polymer $[\mathrm{Mn(pmba)_2}]_n$ (**1**) based on Hpmba has been synthesized and structurally characterized. It has a 3D metal-organic supramolecular framework consisting of double-helix chains. Magnetic analysis indicates weak antiferromagnetic coupling between Mn(II) ions. This study shows that Hpmba is a useful bridging ligand for the construction of coordination polymers with helical structures.

Supplementary Data

CCDC 824906 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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