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Synthesis, structure and magnetic properties of manganese(II) coordination polymer with azido and zwitterionic dicarboxylate ligand

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ABSTRACT

A coordination polymer formulated as {[Mn2L(N3)4]·2H2O}n(1) [L = 1,4-bis(pyridinil-3-carboxylato)l,4-dimethylbenzene] was synthesized and structurally and magnetically characterized. The uniform Mn(II) chains with mixed (μ -EO-N3)2(μ -COO) triple bridges (EO = end-on) are linked by L ligands to generate a 2-fold interpenetrating 3D framework. Meanwhile, magnetism analysis reveals antiferromagnetic coupling for **1**.

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1. Introduction

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Over the past decades, considerable attentions have been paid to rational design and synthesis of novel coordination polymers with intriguing structure and diverse functions [1,2], owing to its promising application as functional materials in many fields [3,4]. As two typical bridging groups affording magnetic clusters and polymers, carboxylate and azido anions have been widely used due to their rich coordination modes as well as diverse magnetic coupling patterns [5–7], and therefore many unique carboxylatecontaining ligands have been developed to construct magnetic coordination compounds.

Recently, some coordination compounds derived from azide and zwitterionic dicarboxylate ligands were reported [7], which demonstrates that using zwitterionic carboxylates as ligands is an efficient synthetic strategy toward mixed azide- and carboxylatebridging systems [7,8]. Normally when zwitterionic carboxylates are used as neutral organic ligands to construct metal–organic compounds, additional anions are necessary for charge balance [9]. Compared with rigid ligands, flexible ligands can form some unique and interesting frameworks because it can freely bend and rotate in the assembly process [8a,10].

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In this paper, we selected 1,4-bis(pyridinil-3-carboxylato)-l, 31 4-dimethylbenzene (L) as organic linker (Scheme 1) and azide as 32 co-ligand to produce a novel 2-fold interpenetrating three 33 dimension (3D) Mn(II) polymer { $[Mn_2L(N_3)_4] \cdot 2H_2O_n$ (1) with 34 anti-ferromagnetism. 35

2. Experimental

Materials and physical measurements: 1.4-Bis(pyridinil-3-37 carboxylato)-l,4-dimethylbenzene (L) was prepared according to 38 the literature [11]. Other chemicals are commercially available 39 and were used as received. Elemental analysis was carried on a 40 Perkin-Elmer 240C analyzer. IR spectrum was measured on a 41 Tensor 27 (Bruker) FT-IR spectrometer with KBr pellets. The X-ray 42 powder diffraction (XRPD) experiments were carried out on a 43 Rigaku D/Max-2500 diffractometer, operated at 40 kV and 100 mA, 44 using a Cu-target tube and a graphite monochromator. Simulation 45 of the PXRD spectra were conducted based on the single-crystal 46 data and diffraction-crystal module of the Mercury (Hg) 47 program available free of charge in Internet (http://www.iucr.org). 48 Magnetic data were collected using crushed crystals of the sample 49 on a Quantum Design MPMS-XL SQUID magnetometer. 50

Synthesis of L:L was prepared in a way similar to that reported51in literature [11]. 1,4-Bis-bromomethylbenzene (1.75 g, 10 mmol)52was dissolved in the acetone solution of ethyl nicotinate (2.83 mL,53

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Scheme 1. The structure of L [L = 1,4-bis(pyridinil-3-carboxylato)-1,4-dimethylbenzene].

54 20 mmol). The mixture was refluxed and filtered to give a white 55 precipitate, which was further hydrolyzed by dilute hydrochloric 56 acid (5%, 50 mL). Then, the bromide ions were removed by fresh 57 silver(I) oxide (prepared by the reaction of AgNO₃ and NaOH in 58 aqueous solution), and white powder of L was obtained (Yield: 80% 59 based on 1,4-bis-bromomethylbenzene). Anal. calcd. for 60 C20H16N2O4 (%): C 68.96, H 4.63, N 8.04. Found (%): C 68.82, H 4.68, N 8.13. IR (KBr, cm⁻¹): 3342(w), 3288(w), 3037(m), 1728(m), 61 62 1640(m), 1301(s), 1130(s), 750(s), 671(s).

Synthesis of $\{[Mn_2L(N_3)_4]\cdot 2H_2O\}_n$ (1): $Mn(ClO_4)_2\cdot 6H_2O$ (0.2 mmol), L (0.15 mmol) and NaN₃ (1 mmol) were added to a mixture solution of C₂H₅OH (4 mL) and H₂O (2 mL). The resulting mixture was sealed in a Teflon-lined autoclave, and heated at 75 °C for 24 h. After cooling to room temperature, yellow block crystal was obtained with a yield of 80% based on L. FT-IR (KBr pellet, cm⁻¹): 3607(s), 3384(m), 3302(m), 2080(s), 1635(m), 1602(w), 1406(w), 1384(s). Element. Anal. Calcd. for C₂₀H₂₀Mn₂N₁₄O₆ (%): C 36.25, H 3.02, N 29.61; Found (%): C 36.22, H 3.01, N 29.59.

Caution! Azido compounds of metal ions are potentially explosive,
 and only a small amount of materials should be prepared with care.

75 Cystallographic Studies: X-ray diffraction data were collected 76 on a SCX-mini diffractometer at 293 K with graphite monochro-77 mated Mo-K α radiation (λ = 0.71073 Å) by an ω scan mode. The 78 program SAINT [12] was used for the integration of the diffraction 79 profiles. Absorption corrections were carried out by using multi-80 scan program SADABS [13]. The structures were solved by direct 81 method and refined by full-matrix least-squares technique using 82 SHELXTL [14]. The positions of metal atoms were located from E-83 maps by direct-method and other non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen 84 85 atoms of the ligands were generated theoretically onto specific atoms and refined isotropically with fixed thermal factors. 86 87 Crystallographic data and structure refinement results are

Table 1

Crystal data and structure refinement parameters for polymer 1	1.
----------------------------------------------------------------	----

Chemical formula	$C_{20}H_{20}Mn_2N_{14}O_6$
Fw	662.35
Space group	<i>P</i> -1
a (Å)	11.129 (2)
b (Å)	11.407 (2)
c (Å)	12.024 (2)
α	63.55 (3)
β	81.91 (3)
γ	78.44 (3)
$V(Å^3)$	1337.8 (5)
Z	2
D (g cm ⁻³)	1.634
μ (mm)	1.009
Temperature (K)	293 (2)
$R^{\rm a}/(wR)^{\rm b}$	0.0547/0.1296
$a = \sum E = E / \sum E $	

 $\mathbf{K} = \sum_{\mathbf{I}} \|\mathbf{I}_{\mathbf{O}}\| = \|\mathbf{I}_{\mathbf{C}}\| / \sum_{\mathbf{I}} \|\mathbf{I}_{\mathbf{O}}\|$

^b $wR = [\sum [w(F_o^2 - F_c^2)] / \sum w(F_o^2)]^{1/2}.$

summarized in Table 1 and selected bond lengths and angles 88 are listed in Table S1 in Supporting information. Crystallographic Q2 89 data (excluding structure factors) for 1 have been deposited in the 90 Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, 91 Cambridge CB21EZ, UK. Copies of the data can be obtained free of 92 charge on quoting the depository number CCDC-996878, the 93 names of the authors, (E-mail: deposit@ccdc.cam.ac.uk, http:// 94 www.ccdc.cam.ac.uk). 95

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3. Results and discussion

Single-crystal X-ray diffraction analysis reveals that 1 crystal-97 lized in triclinic P-1 space group. The asymmetric unit comprises of 98 one crystallographically independent Mn(II) ion (Mn1), two 99 independent halves of Mn(II) ions (Mn2 and Mn3), four azido 100 anions, one L ligand and two uncoordinated water molecules, as 101 displayed in Fig. 1a. Mn1 locates in a disordered coordination 102 environment defined by four azido nitrogen atoms (N1, N4, N7 and 103 N10) and two *cis* carboxylate oxygen atoms (O2 and O3). Mn2 and 104 Mn3 both assume the *trans*-octahedral [N₄O₂] coordination 105 environment defined by four equatorial azido nitrogen atoms 106 (N7, N7B, N10 and N10B for Mn2, N1, N1A, N4 and N4A for Mn3) 107 and two axial carboxylate oxygen atoms (O4 and O4B for Mn2, O1 108 and O1A for Mn3) (Fig. 1b). The Mn-N distances for Mn2 and Mn3 109 (2.195(4)–2.271(4) Å for Mn2 and 2.213(3)–2.214(3) Å for Mn3) 110 are slightly longer than the Mn-O distances (2.167(3) Å for Mn2 111 and 2.211(3) Å for Mn3), indicating an axial elongation of the 112 octahedron. The metal ions alternate in Mn1-Mn2-Mn1-Mn3 113



Fig. 1. View of (a) the asymmetric unit of polymer 1 and (b) the coordination environment of Mn(II) and 1D chain. Hydrogen atoms and water molecules are omitted for clarity. Symmetry codes: (A) -x + 2, -y, -z + 1. (B) -x + 2, -y, -z. (C) -x + 1, -y, -z + 2. (D) -x + 1, -y + 1, -z + 1.

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Fig. 2. (a) Single 3D network. (b) The two-fold interpenetration of network.

sequence and two adjacent metal ions are triply bridged by two EO
(EO = end-on) azido ions and one *syn-syn* carboxylate group, to
generate a uniform chain (Fig. 1b).

117 For the L in 1, the two pyridinium rings adopts trans conformation with respect to the 1.4-dimenthylbenzene, leading 118 119 to a zigzag shape for the ligand. Each chain is linked with adjacent four identical chains through L ligands to give a complicated 3D 120 network (Fig. 2a). Large "empty" space related to the L linkers is 121 122 observed for the single network, but is filled by the 2-fold 123 interpenetration occurred between two equivalent 3D networks 124 (Fig 2b).

The X-ray powder diffraction (XRPD) experiment was per-125 126 formed in order to make sure that the crystal structure is truly 127 representative of the bulk materials. The diffraction intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 5° to 50° 128 with a step size of 0.02° and a scan speed of 8° min⁻¹. The 129 130 experimental diffraction pattern and the simulated pattern are shown in Fig. 3. Good consistence between the experimental 131 132 pattern and the simulated pattern as displayed in Fig. 3 indicates 133 that bulk-synthesized materials and the as-grown crystals are 134 homogeneous.

The solid state magnetic susceptibility of polymer **1** was measured in 2–300 K at a field of 1 kOe, and the dependence of magnetic susceptibility on temperature was plotted in $\chi_m T vs$ T profile (Fig. 4a) and $\chi_m^{-1} vs T$ (Fig. S1). The $\chi_m T$ value per Mn(II) at 300 K (3.96 emu K mol⁻¹) is lower than the spin-only value (4.38 emu K mol⁻¹) expected for a magnetically isolated



Fig. 3. X-ray powder diffraction (XRPD) patterns for 1.

high-spin Mn(II) ion (g = 2.0), which reveals the presence of anti-141 ferromagnetic (AF) coupling in this polymer. The shape of $\chi_m T$ plot 142 (Fig. 4a) implies the AF interaction between the Mn(II) ions in 1, 143 which is corroborated by the large negative Weiss constant 144 θ = -68 K deduced from the Curie-Weiss fitting of the $\chi_{\rm m}^{-1}$ vs T 145 data above 50 K (Fig. S1 in Supporting information). The field-146 dependent magnetization at 2 K shows a linear increasing trend 147 and reaches 0.61 N β at 7 T (Fig. 4b), which is much smaller than 148 the saturated vale 5 N β expected for one Mn(II) ion with g = 2.0 149 and S = 5/2 and further confirms the AF coupling of **1**. 150

The global AF behavior of 1 can be interpreted by magneto-151 structural relationship. The Mn(II) ions in **1** are bridged by EO azido 152 and syn,syn carboxylate of L ligand. It is well known that syn,syn 153 carboxylate mediates AF interaction, while the nature of the 154 coupling transmitted by EO mode depends on the M-Nazido-M 155 angle [5c]. For Mn(II) ions, the ferromagnetic coupling appears over 156 the crossover angle of 98° and reaches its top at 106° [5c]. In 157 polymer 1, the bridging angle of EO azido is 94.69° for Mn(1)-N(4)-158 Mn(3) and 95.08° for Mn(1)-N(1)-Mn(3); while the bridging angle 159 of EO azido is 94.27° for Mn(1)-N(7)-Mn(2) and 93.12° for Mn(1)-160 N(10)–Mn(2). All of these angles are smaller than 98° and therefore 161 conduct AF coupling. The AF exchange interaction mediated by EO 162 azido and syn,syn carboxylate of L ligand should account for the 163 global AF behavior of **1**. 164

Complex 1 can be magnetically considered as an infinite 165 uniform chain in which the magnetic coupling is mediated through 166 the mixed $(\mu$ -EO-N₃)₂ $(\mu$ -COO) triple bridges. The interchain 167 interactions via the long L ligand could be ignored. Considering 168 that the chain contains two sets of triple bridges with different 169 structural parameters that alternating in AABB sequence, it 170 should be described as a 1D Heisenberg chain with alternating 171 $J_1-J_1-J_2-J_2$ interactions. The corresponding Hamiltonian is 172 $H = -J_1 \Sigma (S_{4i-2} S_{4i-1} + S_{4i-1} S_{4i}) - J_2 \Sigma (S_{4i} S_{4i+1} + S_{4i+1} S_{4i+2}) \text{ and the}$ 173 expression of χ for such a chain in the classical-spin approximation 174 was exported as follows [15]: 175

$$\chi_{\text{chain}} = \left[\frac{Ng^2\beta^2S(S+1)}{12kT}\right] \left(\frac{A}{B}\right)$$

176

where $A = 4 + 4u_1 + 4u_2 + 4u_1u_2 + 2u_1^2 + 2u_2^2 + 4u_1^2 u_2 + 4u_1u_2^2 + 178$ $4u_1^2u_2^2$ and $B = 1 - u_1^2u_2^2$. The *u* is the Langevin function u = 179 $\operatorname{coth}[JS(S+1)/kT] - kT/[JS(S+1)]$ with S = 5/2. The best simulation 180

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Q4 Fig. 4. (a) The χ_mT vs T plot of 1. The solid red lines represent the best fits to the uniform-chain model. (b) The M vs H plot of 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

gives rise to $J_1 = -9.889 \text{ cm}^{-1}$, $J_2 = -4.697 \text{ cm}^{-1}$ and g = 2.02. Different *J* values indicate that appreciably different magnetic 181 182 183 interactions are mediated through different triple bridges, while 184 negative *J* values reconfirm the AF coupling of **1**.

185 4. Conclusion

186 A Mn(II) coordination polymer with a 2-fold interpenetrating 187 3D framework based on azide ion and zwitterionic dicarboxylate 188 was synthesized under hydrothermal conditions. Furthermore,

189 magnetism analysis reveals anti-ferromagnetism for 1.

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