

Article

Two Polynuclear Manganese(II) Complexes Based on Multidentate N-Heterocyclic Aromatic Ligand and V-Shaped Polycarboxylate Ligand: Synthesis, Crystal Structure Analysis and Magnetic Properties

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Abstract: The reaction of MnCl_2 , 2-(5-{6-[5-(Pyrazin-2-yl)-1H-1,2,4-triazol-3-yl]pyridin-2-yl}-1H-1,2,4-triazol-3-yl)pyrazine (H_2ptptp), 4,4'-sulfonyldibenzoic acid (H_2sdba) or 4-(4-carboxyphenoxy)phthalate acid (H_3cpop) and [BMI]Br ionic liquids (BMI = 1-butyl-3-methylimidazolium) gave rise to two complexes, $[\text{Mn}_4(\text{ptptp})_2(\text{sdba})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Mn}_3(\text{ptptp})(\text{cpop})\text{Br}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**2**). The compounds have been well characterized by elemental analysis, IR spectra, thermogravimetric analysis, as well as single-crystal and powder X-ray diffraction. The structure feature of **1** is that Mn(II) ions in the $[\text{Mn}_6(\text{sdba})_2]$ loops of V-shaped sdba^{2-} ligands are ptptp^{2-} ligands, respectively, and a 2D layer is constructed from sdba^{2-} and ptptp^{2-} ligands. The adjacent 2D layers are connected by $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds to form a 3D supramolecular network. The neighbouring trinuclear Mn(II) clusters in **2** are linked by V-shaped cpop^{3-} ligands to give a 2D layer, which is penetrated by ptptp^{2-} ligands to form self-threading structure. The results of variable-temperature magnetic studies have shown that the magnetic interactions between the Mn(II) ions in **1** and **2** are mainly due to antiferromagnetic coupling.

Keywords: manganese(II) coordination polymer; ionic liquid; self-threading; magnetism



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1. Introduction

Recently, extensive research on the design and synthesis of multi-core complexes has led to many practical and conceptual developments [1]. Many reports have shown that polynuclear complexes with relatively simple spatial structures have excellent properties, which may provide an opportunity for a better understanding of structure related properties [2,3]. So far, the selective adsorption, catalysis and magnetism of multi-core complexes have proved to be very attractive [4,5]. Ligands containing 1,2,4-triazole are considered to be interesting heterocyclic compounds because of their strong coordination ability to transition central metal ions and effective biological significance [6–8]. 1,2,4-triazole ligands are usually easy to coordinate with the metal ions by the N1, N2 atoms [9] to produce polynuclear complexes. The length of metal ion chains in the polynuclear complexes changed from a binuclear, trinuclear, to polynuclear linear-chain [10–12]. The 1,2,4-triazole and its pyrazine derivative, 2-(5-{6-[5-(Pyrazin-2-yl)-1H-1,2,4-triazol-3-yl]pyridin-2-yl}-1H-1,2,4-triazol-3-yl)pyrazine (H_2ptptp), have often been used as the linker based on the following considerations: (i) nitrogen atom chelation coordination; (ii) more potential coordination points (bidentate, tridentate or tetradentate) and coordination modes; (iii) regardless of the conformation, H_2ptptp can provide potential tridentate and bidentate binding sites via rotation around the central C–C bond [13].

Traditional synthetic methods of coordination polymers (CPs) are hydrothermal and solvothermal methods. In addition, as an important synthesis method, ionothermal synthesis has been successfully introduced to the preparation of coordination polymers [14–16].

In this synthetic method, ionic liquids (ILs) act as the solvents, potential templates, or structural directing agents in the formation of coordination polymers. Compared with the hydrothermal and solvothermal methods, this method has the following advantages: Firstly, ILs possess better solubility to most of the inorganic precursors, which can greatly improve the reactivity of the species in the reaction system. Secondly, ILs have lower vapor pressures at room temperature or elevated temperature, which means coordination polymers can be prepared at higher temperature. Thirdly, ILs have higher chemical and thermal stabilities, and lower toxicities, so they can be used as substitute for all or part of toxic organic solvents. We have successfully synthesized a series of Mn(II) coordination complexes based on H₂ptptp and bridging carboxylate ligands, in which [RMI]Br (RMI = 1-alkyl-3-methylimidazolium, R = ethyl, or propyl, or butyl) ILs could play a structure directing role and were intimately involved in template ordering the final structure [17,18].

To continue our study concerning the influence of [RMI]Br ILs on synthesizing Mn(II) CPs based on bridging carboxylate ligands, we still select H₂ptptp as the main ligand in the self-assembly process. In this study, we present two new polynuclear complexes {[Mn₄(ptptp)₂(sdba)₂(H₂O)₂]·2H₂O}_n (**1**) and {[Mn₃(ptptp)(cpop)Br(H₂O)₂]·2H₂O}_n (**2**) prepared by [BMI]Br ILs ([BMI]Br = 1-butyl-3-methylimidazolium bromide) based on V-shaped bi-carboxylate ligand 4,4'-sulfonyldibenzoic acid (H₂sdba) and tricarboxylate ligand 4-(4-carboxyphenoxy)phthalate acid (H₃cpop) respectively. The two complexes have been well characterized by single-crystal and powder X-ray diffraction, elemental analysis, infrared spectroscopy, thermogravimetric analysis, and variable temperature magnetic susceptibility.

2. Materials and Methods

2.1. Reagents and Instruments

H₂ptptp ligand was purchased from China Jinan Henghua Sci. & Tec. Co. Ltd. (Henghua, Jinan, China). [RMI]Br ILs were purchased from the Center for Green Chemistry and Catalysis (Lanzhou Institute of Chemical Physics Chinese Academy of Sciences, Lanzhou, China). All other reagents are analytical grade reagents and were obtained from commercial sources without further purification. Elemental analyses for C and H were performed on a Perkin-Elmer 240 elemental analyzer (PerkinElmer, Waltham, MA, USA). The FT-IR spectra were recorded from KBr pellets in the range from 400 to 4000 cm^{−1} on a Bruker VECTOR 22 spectrometer (Bruker, Bremen, Germany). Thermal analyses were performed on a SDT 2960 thermal analyzer (TA, Newcastle, DE, USA) from room temperature to 800 °C, heating rate of 20 K min^{−1}, under nitrogen flow. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/Max 3III diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation (λ = 1.5406 Å), in the 2θ range of 5–50°, with a scan speed of 4° min^{−1} at room temperature. The variable-temperature magnetic susceptibilities of samples were measured using a MPMS-7 SQUID magnetometer (QuantumDesign, San Diego, CA, USA).

2.2. Single-Crystal X-Ray Diffraction

By using φ/ω scan technique, single crystal X-ray diffraction analysis of **1** was carried out on a Bruker SMART APEX II CCD diffractometer (Bruker, Bremen, Germany) at the temperature of 20 ± 1 °C, which was equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystallographic data of **2** were collected on Rigaku Saturn 724 CCD diffractometer (Mo-Kα, λ = 0.71073 Å, Rigaku, Tokyo, Japan) at temperature of 20 ± 1 °C. These structures take Olex2 program as the interface and are solved together with SHELXT and SHELXL programs [19,20]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. CCDC 2133345 and 2144091 contain the supplementary crystallographic data for **1** and **2**, respectively. Crystal data and structure processing parameters for **1–2** are summarized in Table 1. Selected bond lengths and bond angles of **1–2** are listed in the Supplementary Materials Table S1.

Table 1. Crystallographic parameters for compounds 1–2.

Compound	1	2
Formula	C ₆₂ H ₄₂ Mn ₄ N ₂₂ O ₁₆ S ₂	C ₃₂ H ₂₂ BrMn ₃ N ₁₁ O ₁₀
Formula weight	1635.06	965.34
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
<i>a</i> (Å)	20.435(4)	11.454(2)
<i>b</i> (Å)	16.136(3)	12.093(2)
<i>c</i> (Å)	21.182(4)	14.054(3)
α (°)	90	106.93(3)
β (°)	91.315(2)	91.07(3)
γ (°)	90	99.90(3)
<i>V</i> (Å ³)	6983(2)	1829.9(6)
<i>Z</i>	4	2
<i>D</i> _{calc} (g·cm ^{−3})	1.555	1.752
μ (mm ^{−1})	0.850	2.184
<i>F</i> (000)	3312	962
θ range for data collection (°)	2.30/25.50	1.97/25.50
Data/restraints/parameters	12997/6/955	6694/12/523
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b	<i>R</i> ₁ = 0.0620	<i>R</i> ₁ = 0.0597
(<i>I</i> > 2 σ (<i>I</i>))	<i>wR</i> ₂ = 0.1843	<i>wR</i> ₂ = 0.1569
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.0683	<i>R</i> ₁ = 0.1184
	<i>wR</i> ₂ = 0.1903	<i>wR</i> ₂ = 0.1921
GOF	1.019	1.063

$$^a R = [\sum ||F_0| - |F_c|| / \sum |F_0|], ^b R_w = \sum_w [|F_0|^2 - F_c^2|^2 / \sum_w (|F_w|^2)]^{1/2}.$$

2.3. Preparation of Compounds 1–2

2.3.1. Synthesis of {[Mn₄(ptptp)₂(sdba)₂(H₂O)₂]}·2H₂O)_{*n*} (1)

MnCl₂·4H₂O (0.1 mmol, 19.8 mg), H₂ptptp (0.05 mmol, 18.4 mg), H₂sdba (0.1 mmol, 30.6 mg), and 1.3 g [BMI]Br ILs were dissolved in 10 mL premixed solvent (CH₃CN/H₂O, *v/v*, 7:3). Then, the mixed solution was placed in a 20 mL Teflon-lined stainless steel container, and the container was sealed and heated to 160 °C for 72 h. After the mixture had been cooled down to room temperature at a rate of 5 °C·h^{−1}, yellow crystals of **1** were obtained with a yield of 76% (based on Mn). Anal. Calc for C₆₂H₄₂Mn₄N₂₂O₁₆S₂ (%): C, 45.54; H, 2.59; N, 18.85. Found: C, 45.43; H, 2.52; N, 18.73. IR (cm^{−1}, KBr): 3428 s, 1594 s, 1552 s, 1500 w, 1404 s, 1189 m, 1012 w, 846 w, 743 m, 616 s. Note that **1** could also be obtained without [BMI]Br added, but the yield is only 34%, which is lower than that in the presence of [BMI]Br ILs.

2.3.2. Synthesis of {[Mn₃(ptptp)(cpop)Br(H₂O)₂]}·2H₂O)_{*n*} (2)

The same synthetic method as that for **2** was used except that H₂sdba was replaced by H₃cpop (0.1 mmol, 30.2 mg). Yield: 89% (based on Mn). Anal. Calc for C₃₂H₂₂BrMn₃N₁₁O₁₀ (%): C, 39.82; H, 2.30; N, 15.96. Found: C, 39.68; H, 2.23; N, 15.82. IR (cm^{−1}, KBr): 3421 s, 1596 s, 1542 s, 1500 m, 1378 s, 1195 m, 1143 m, 950 w, 747 w, 661 w. Note that **2** could not be obtained without [BMI]Br ILs added.

For the purpose of exploring the reaction mechanism and optimizing the reaction conditions of **2**, a series of experiments were conducted to determine the effects of [BMI]Br. First, when other bromide salts, such as NaBr, KBr, or MnBr₂, were selected to replace [BMI]Br separately, **2** could not be obtained. Only unspecified impurities can be found, not any crystals. However, when the cation of the ILs altering from [BMI]⁺ to [EMI]⁺ ([EMI]⁺ = 1-ethyl-3-methylimidazolium) or [PMI]⁺ ([PMI]⁺ = 1-propyl-3-methylimidazolium), **2** could also be successfully obtained. The additive amount of [BMI]Br ILs is derived from our previous work [18].

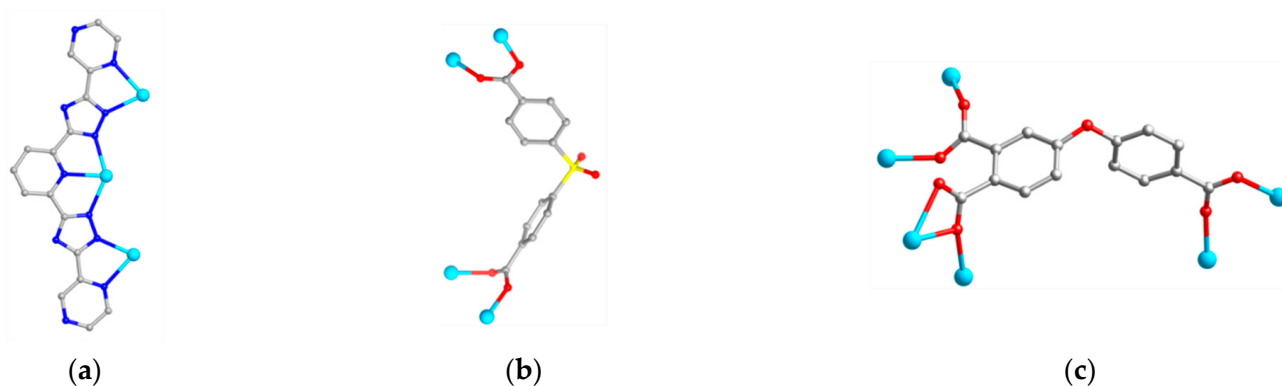
3. Results and Discussion

3.1. Structural Description

3.1.1. Crystal Structure of 1

Complex **1** crystallizes in the monoclinic space group $P2(1)/c$. As depicted in Figure 1a, the asymmetric unit of **1** contains four crystallographic independent Mn(II) ions, two completely deprotonated ptptp^{2-} ligands, two sdba^{2-} ligands, two coordinated water molecules and two free water molecules. The four Mn(II) ions can be divided into two types: central (Mn1 and Mn2) and terminal (Mn3 and Mn4). The central Mn1 and Mn2 ions have a distorted octahedral $\{\text{N}_3\text{O}_3\}$ coordination geometry derived from the tridentate site of one ptptp^{2-} ligand, two carboxylate oxygen atoms from two sdba^{2-} ligands, and one coordinated water molecule, whereas the terminal Mn3 and Mn4 ions have a distorted octahedral $\{\text{N}_4\text{O}_2\}$ coordination geometry derived from two terminal bidentate bonding sites of two ptptp^{2-} ligands and two carboxylate oxygen atoms of two sdba^{2-} ligands. The angle between the planes defined by the two N–Mn–N chelate rings at Mn3 is $71.60(14)^\circ$ and at Mn4 is $76.29(15)^\circ$, respectively. The bite angles of bidentate bonding units at Mn3 are $70.05(15)^\circ$ and $72.00(15)^\circ$, and at Mn4 are $71.71(16)^\circ$ and $69.76(16)^\circ$, respectively.

Interestingly, two kinds of helices in **1** were found within the bonds between the Mn(II) ions and ptptp^{2-} ligands (Figure 1b). Using its central tridentate and terminal bidentate binding sites, each ptptp^{2-} ligand adopt the syn–syn coordination mode (Scheme 1a) and bridge adjacent Mn(II) ions to form charming helical chains with left-handed and right-handed helical rings. The pitch of the left-handed spiral and the right-handed spiral along the b-axis is equal to the length of the b-axis. In the right $(\text{Mn}-\text{ptptp})_n$ helix, the adjacent Mn ... Mn distances are $4.4918(13)$ Å for Mn4–Mn2 and $4.6183(13)$ Å for Mn2–Mn4#2, respectively. Moreover, in the left $(\text{Mn}-\text{ptptp})_n$ helix, the adjacent Mn ... Mn distance are $4.5064(14)$ Å for Mn3–Mn1 and $4.5608(13)$ Å for Mn1–Mn3#1, respectively.



Scheme 1. Coordination mode of ptptp^{2-} (**1** and **2**, for (a)), sdba^{2-} (**1**, for (b)), and cpop^{3-} (**2**, for (c)) ligands, color code: C gray, N blue, O red, S yellow, Mn turquoise.

As an important semi-rigid dicarboxylic acid ligand, H_2sdba can be considered to be conducive to the preparation of mixed ligand polynuclear complexes [21–23]. In **1**, all the H_2sdba ligands are completely deprotonated and adopt bis-bidentate bridging coordination mode (Scheme 1b). That is to say, each sdba^{2-} ligand acts as a tetra-connector linking four Mn(II) ions. Two Mn atoms are joined by two sdba^{2-} ligands to form a bi-nucleated Mn(II) cluster as a secondary building unit (SBU) with a $\text{Mn1} \cdots \text{Mn3}$ and $\text{Mn2} \cdots \text{Mn4}$. These SBUs can be further extended by the carboxylate groups of the sdba^{2-} ligands to give a 2D helix layer (Figure 1c). The interesting feature is that Mn(II) ions in the $[\text{Mn}_6(\text{sdba})_2]$ loops of V-shaped sdba^{2-} ligands are ptptp^{2-} ligands, respectively and 2D layer constructed from sdba^{2-} and ptptp^{2-} ligands (Figure 1d). The adjacent 2D layers are connected by linking to the $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds between the O atoms from water molecules and the N atoms of the pyridine rings, the forces acting between sdba^{2-} form a 3D supramolecular network (Figure 1e). In order to make the structure more intuitive, the left helix of ptptp^{2-} was defined as purple, the right helix was defined as green, the two adjacent sdba^{2-} ligands

form a rhombic were defined as light blue, and the simplified sketch of the entire 3D structure is illustrated in Figure 1f.

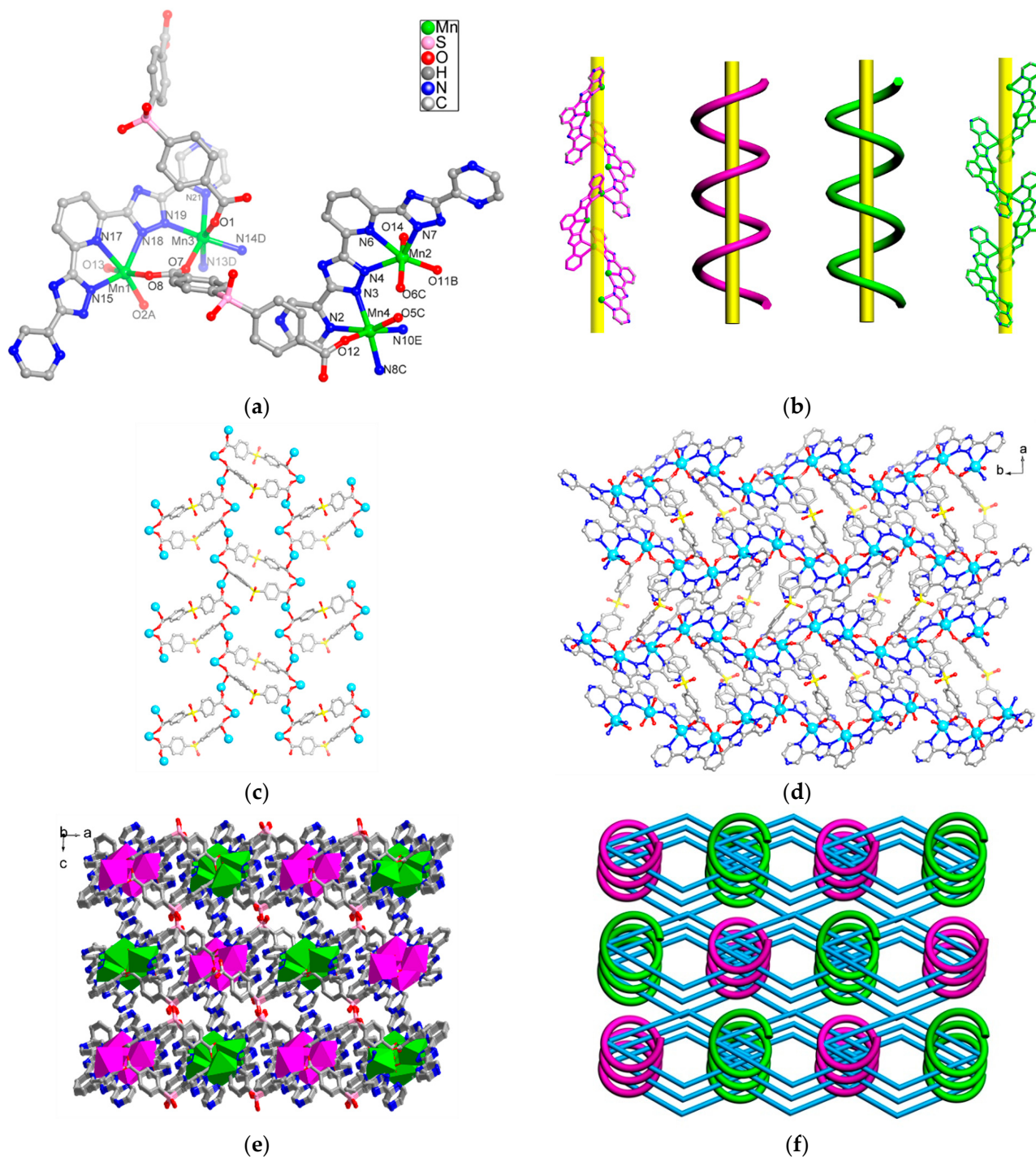


Figure 1. (a) Local coordination environment of Mn(II) ions in **1**. (b) Left- and right-stranded helices constructed from ptp²⁻ ligands. (c) 2D layer constructed by sdba²⁻ ligands. (d) 2D layer constructed by sdba²⁻ and ptp²⁻ ligands. (e) Perspective view of 3D supramolecular framework. (f) The simplified sketch of the entire 3D structure.

3.1.2. Crystal Structure of **2**

Complex **2** crystallizes in the triclinic space group *P*-1 and exhibits a 2D 4-connected network based on trinuclear cluster. Each asymmetric unit of **2** contains three Mn(II) ions, one completely deprotonated ptp²⁻ ligand, one cpop³⁻ anion, and two coordinated

water molecules. As shown in Figure 2a, the Mn1 atom is five-coordinated, adopting a distorted trigonal bipyramid geometry via coordinating to three carboxylate oxygen atoms from three cpop^{3−} ligands and two nitrogen atoms from one ptptp^{2−} ligand. Mn2 atom is coordinated by three nitrogen atoms from one ptptp^{2−} ligand, one carboxylate oxygen atom, and two oxygen atoms from two coordinated water molecules to finish a distorted octahedral geometry. Mn3 atom is coordinated by two nitrogen atoms from the only ptptp^{2−} ligand, two carboxylate oxygen atoms from two cpop^{3−} ligands, one bromide ion to finish distorted octahedral geometry. All the Mn–O [range of 2.048(4)– 2.435(4) Å] and Mn–N [range of 2.158(4)– 2.423(5) Å] bond distances are in the normal range [24,25].

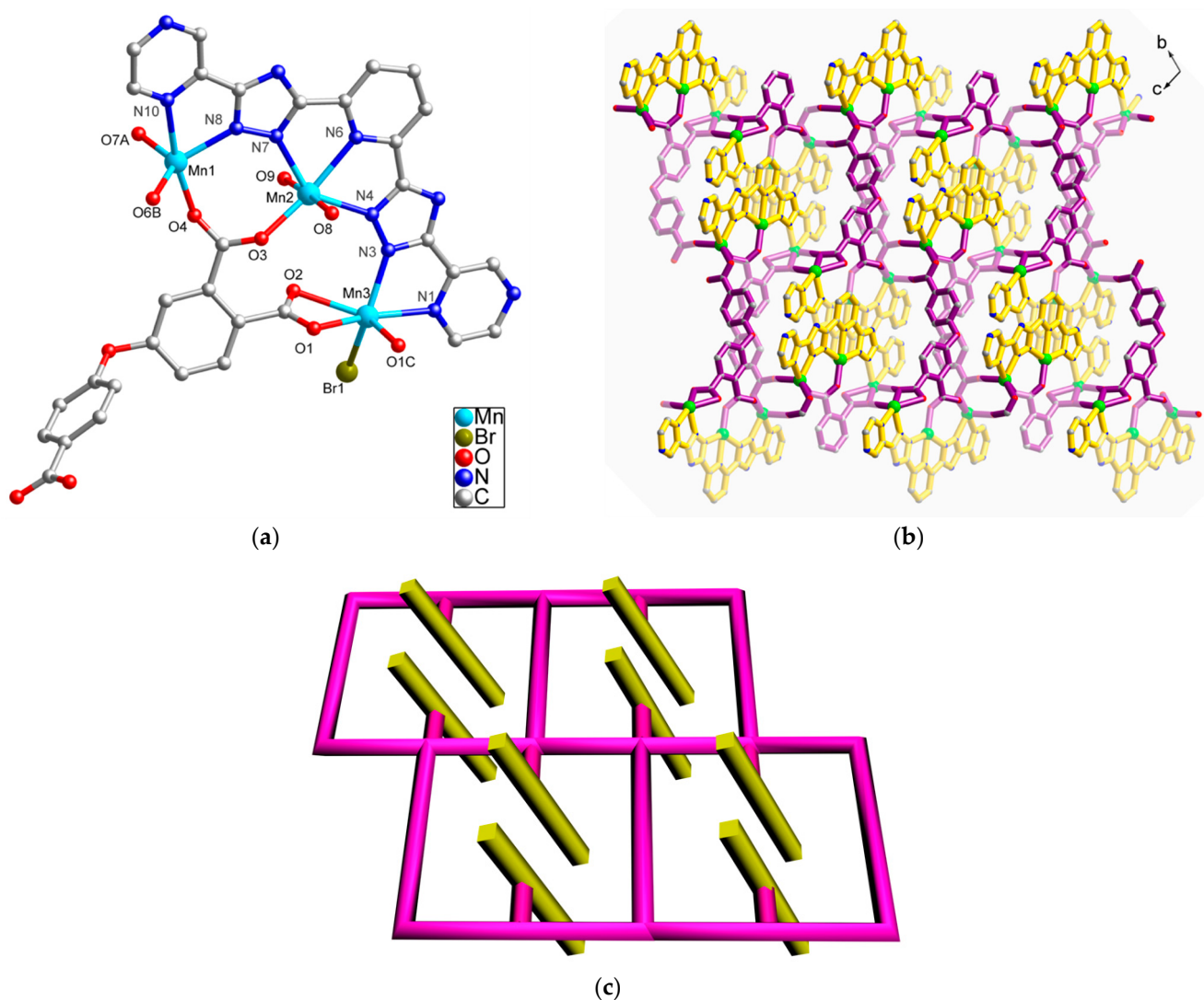


Figure 2. (a) Local coordination environment of Mn(II) ions in **2**. (b) 2D self-threading architecture in **2**. (c) Schematic diagram of the 2D self-threading structure, the coordinated ptptp^{2−} ligands like inserted wedges are highlighted by ash blonde.

The completely deprotonated cpop^{3−} ligands in **2** all act as a μ_7 -bridging, linking six Mn(II) atoms through μ_2 - η^1 : η^1 , μ_3 - η^1 : η^2 , μ_2 - η^1 : η^1 coordination modes for three carboxylate groups, respectively (Scheme 1c). Three Mn atoms are joined by four cpop^{3−} ligands to form a tri-nucleated Mn(II) cluster as a SBU with Mn1...Mn2 and Mn2...Mn3 (Figure S1). The distances between adjacent Mn...Mn are 4.4131(19) Å for Mn1–Mn2 and 4.5425(19) Å for Mn2–Mn3. The neighbouring trinuclear Mn(II) clusters are actually linked by V-shaped cpop^{3−} ligand spacers to give a 2D layer. The dangling ptptp^{2−} ligand grafted on the trinuclear Mn(II) clusters crosses over the rhombic cavity in the two-

dimensional layer. Each rhombic window is penetrated by two ptptp^{2-} ligands belonging to the two-dimensional layer itself, as shown in Figure 2b. A schematic illustration of the two-dimensional self-threading structure is presented in Figure 2c.

3.2. Powder X-Ray Diffraction (PXRD) and Thermal Analyses

The powder X-ray diffraction (PXRD) pattern of **1** and **2** were checked at room temperature. To present more clearly for a proper judgement of the phase purity, we narrowed the 2θ range (5–40 deg) to display relevant data only. As shown in Figure 3a,b, the experimental PXRD spectrum is consistent with the simulated PXRD spectrum, showing good phase purity of **1** and **2**. It should be noted that the PXRD pattern of **1** must be measured with a freshly prepared sample. When the sample is placed in the air for more than 14 days, the crystallinity of **1** will deteriorate (Figure S2). In order to fully characterize the thermal stability of the complexes, their thermal behaviors in dry nitrogen atmosphere were studied by thermogravimetric analysis (TGA) from 30 to 800 °C. As shown in Figure 3c, a first weight loss of 3.9% occurs from 98 to 170 °C, which corresponds to the loss of coordinated and guest water molecules (calcd: 4.4 %). The main framework of **1** begun to collapse since about 466.0 °C. Further heating to 800 °C indicates a slow weight loss of residue and final residue (22.6%). The last weight loss of 1.8% is observed. **2** begins to collapse from about 156.8 °C, and an initial weight loss of 6.9% is observed, corresponding to the release of coordinated and guest water molecules (calculated, 7.5%). The main framework of **2** begun to collapse at about 418.6 °C. Further heating to 800 °C indicates a slow weight loss of residue and final residue (24.8%).

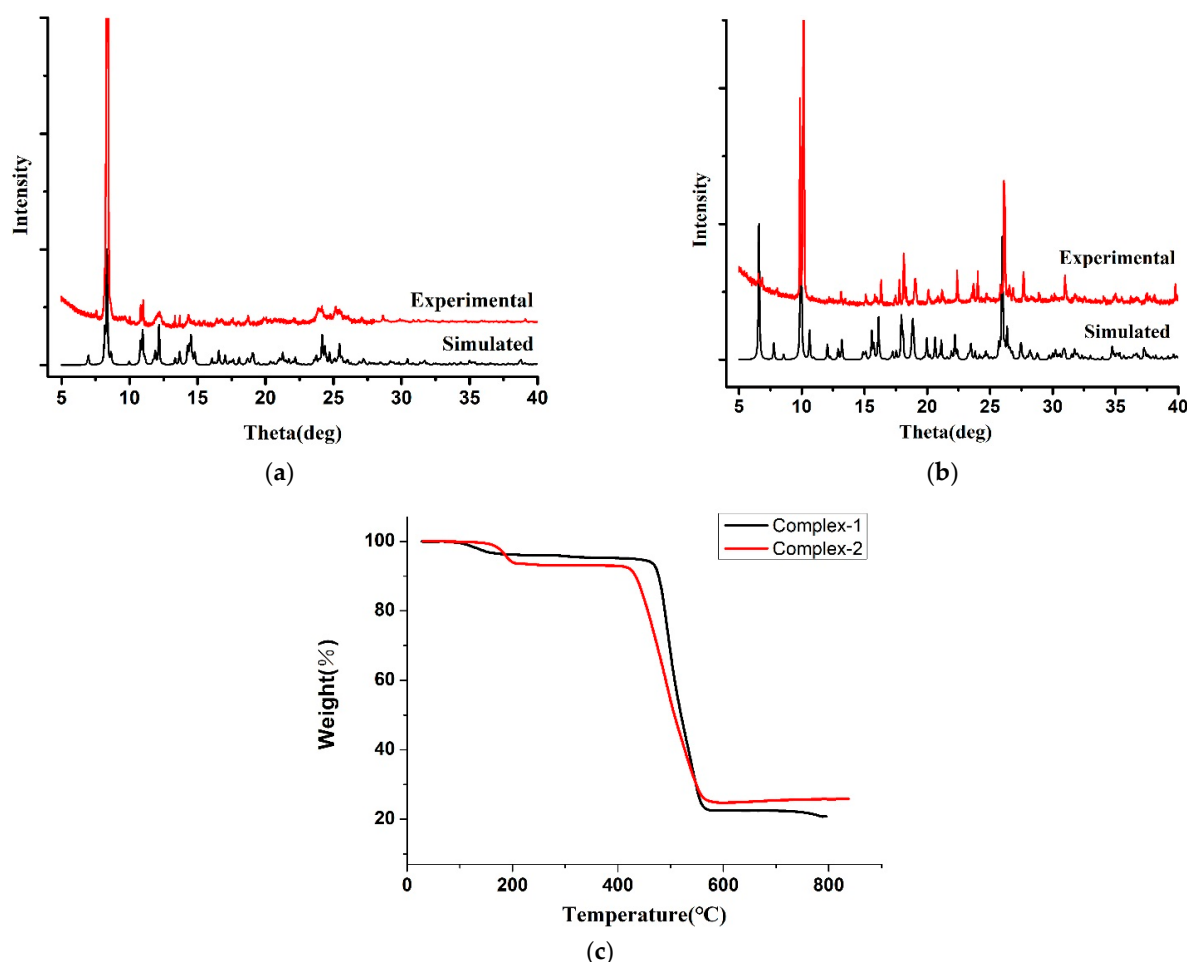


Figure 3. Simulated and experimental PXRD pattern of **1** (a) and **2** (b). Thermogravimetric (TG) analysis curve of **1** and **2** (c).

3.3. Magnetic Properties

In the 2–300 K temperature range, the magnetic susceptibilities of **1** and **2** were measured. The plots of χ_M and $1/\chi_M$ vs. T are shown in Figure 4. For **1**, the experimental $\chi_M T$ values at room temperature is $16.66 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 5.77 \mu_B$), which is lower than the pure spin value $17.52 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 5.92 \mu_B$ and with $g = 2.0$) of four magnetically isolated high spin Mn(II) ions. The 2D structure of **1** was through the use of sdba^{2-} ligands to link the 1D Mn(II) ion chains. In general, sdba^{2-} can form a very weak coupling, so the magnetic behavior shows the characteristics of a one-dimensional chain, the connection mode between Mn(II) ions is carboxylate bridges and $[\text{ptptp}]^{2-}$ -N,N bridges. For **2**, the experimental $\chi_M T$ at room temperature is $4.37 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 5.91 \mu_B$), which is equivalent to the spin only value $4.38 \text{ cm}^3 \text{ K mol}^{-1}$ ($\mu_{\text{eff}} = 5.92 \mu_B$ and with $g = 2.0$) expected for a magnetically isolated high spin Mn(II) ion. The gradual decrease trend of the $\chi_M T$ as the temperature lowering indubitably indicate the antiferromagnetic interactions in **2**. Similar to **1**, the 2D structure of **2** was through the use of cpop^{3-} ligands to link the 1D Mn(II) ions chains.

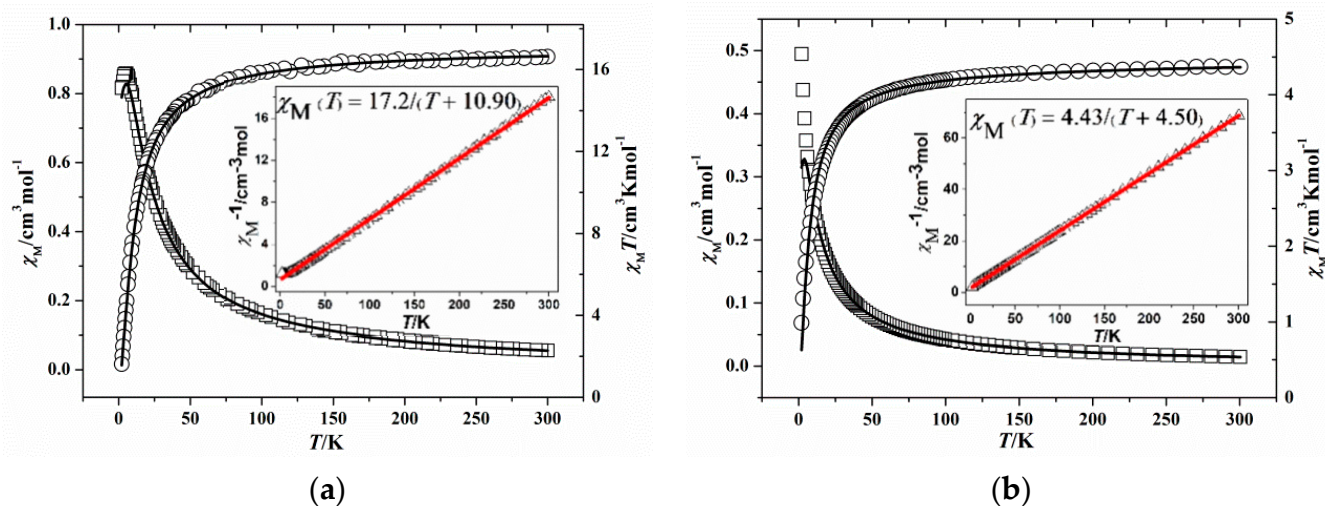


Figure 4. Plots of $\chi_M T$ ($\square$) and χ_M ($\circ$) versus T for complex **1** (a) and **2** (b). Inset: the red line represent the best fit of $1/\chi_M$ based on Curie-Weiss law in 2–300 K temperature range for complex **1** and **2**, respectively.

In the reciprocal susceptibilities ($1/\chi_M$) versus temperature (T) plot (inset in Figure 4), the observed susceptibility data above 10 K were well-fitted by Curie-Weiss law, yielding $C_m = 17.2 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -10.90 \text{ K}$ and $R = 1.29 \times 10^{-4}$ for **1**, and $C_m = 4.43 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -4.50 \text{ K}$ and $R = 2.29 \times 10^{-4}$ for **2**. The negative θ value indicated the presence of weak intrachain antiferromagnetic exchange in complex **1** and **2**.

From a magnetic point of view, **1** and **2** can be regarded as a 1D Mn(II) ion chain. The magnetic exchange pathway in the 1D chain can be considered as a magnetic two Mn(II) chain with the periodic $-J_1 J_2 J_1 J_2$ -coupling sequence. To estimate the magnitude of the antiferromagnetic coupling, the magnetic susceptibility data were fitted according to the spin-exchange Hamiltonian for the alternating chains in **1** and **2**, as follows: $H = -J_1 \sum S_{2i} S_{2i+1} - J_2 \sum S_{2i+1} S_{2i+2}$. The magnetic susceptibility equation of this dimer system is as follows [26]:

$$\chi_M = \frac{Ng^2\mu_B^2}{3kT} \left(\frac{1 + \mu_1 + \mu_2 + \mu_1\mu_2}{1 - u_1^2 u_2^2} \right)$$

$$u_1 = \coth[J_1/kT] - kT/J_1$$

$$u_2 = \coth[J_2/kT] - kT/J_2$$

The best fitting parameters obtained were $J_1 = -0.45$, $J_2 = -1.42$, $g = 1.98$, and $R = 3.23 \times 10^{-3}$ for **1**, and $J_1 = -0.45$, $J_2 = -0.81$, $g = 2.01$, and $R = 3.59 \times 10^{-4}$ for **2** in the 2–300 K temperature range.

4. Conclusions

Two poly-nucleated Mn(II) cluster complexes **1** and **2** with the ligand 2-(5-{6-[5-(Pyrazin-2-yl)-1H-1,2,4-triazol-3-yl]pyridin-2-yl}-1H-1,2,4-triazol-3-yl)pyrazine (H_2ptptp) and V-shaped bicarboxylate ligand H_2sdba or tricarboxylate ligand H_3cpop , respectively, have been synthesized using [BMI]Br ILs as the medium for the preparation. The structure feature of **1** is that Mn(II) ions in the $[Mn_6(sdba)_2]$ loops of V-shaped $sdba^{2-}$ ligands are $ptptp^{2-}$ ligands, respectively and 2D layer is constructed from $sdba^{2-}$ and $ptptp^{2-}$ ligands. The adjacent 2D layers are connected by O–H $\cdots$ N hydrogen bonds to form a 3D supramolecular network. The neighbouring trinuclear Mn(II) clusters in **2** are actually linked by V-shaped $cpop^{3-}$ ligand spacers to give a 2D layer, which is penetrated by $ptptp^{2-}$ ligands to form a self-threading structure. The results of variable temperature magnetic studies show that the magnetic interactions between the Mn(II) ions in **1** and **2** are mainly due to antiferromagnetic coupling.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12020278/s1>. Table S1: Selected bond lengths (Å) and bond angles (°) for **1–2**, Figure S1: The 4-connected network and tri-nucleated Mn(II) cluster of complex **2**. Figure S2: Simulated and experimental PXRD pattern of **1** placed in the air for more than 14 days.

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