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Hydrothermal synthesis, crystal structure and magnetic properties of a new 3D Mn^{II} complex based on the flexible ligand 5-(4-pyridyl)methoxyisophthalic acid

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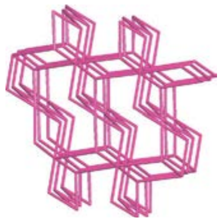
A new 3D coordination polymer $[Mn_2L_2(H_2O)_2\cdot 2DMF\cdot 2H_2O]_n$ [H_2L = 5-(4-pyridyl)methoxyisophthalic acid] with a $\{4^2.6\}_2\{4^4.6^2.8^7.10^2\}$ net has been synthesized from H_2L by a hydrothermal method. Magnetic susceptibility measurements indicated antiferromagnetic interaction between the adjacent Mn^{II} ions in the polymer.



Organic/inorganic functional heterostructures are of interest since they exhibit their own properties or contribute to new physical phenomena and novel applications.[1–5] Among them, coordination polymers have been a subject of intense research activity in recent years due to their potential employment in the areas of magnetism, sensors, gas adsorption, ion exchange and catalysis.[6–9] However, an effective and facile method for the design of two-dimensional (2D) and three-dimensional (3D) metal supramolecular species still remains a big challenge. Among various organic ligands, the flexible ligands have drawn attention because of their interesting topologies, multidimensional networks and attractive properties.[10] The conformational freedom nature of the flexible ligand may provide more possibilities for the construction of unusual topology structures and microporous coordination polymers than single rigid ligands. Recently, we selected the flexible ligand 5-(4-pyridyl)methoxyisophthalic acid (H_2L)[11] as an excellent candidate for the preparation of functional coordination polymers owing to the following characteristics: first, H_2L adopts various coordination modes when it coordinates to metals and thus may produce various structural topologies due to the presence of both carboxylate and pyridine nitrogen donors; second, the *syn–syn* mode of the carboxylic groups can propagate magnetic super exchange between metal centers.

Keeping in mind the above points, we synthesized a new metal–organic polymer based on the Mn^{II} ion and H_2L by a hydrothermal method. The synthesis, crystal structure and magnetic properties of the new 3D polymer $[Mn_2L_2(H_2O)_2\cdot 2DMF\cdot 2H_2O]_n$ **1** were studied in detail.

Colorless block crystals of **1** were obtained hydrothermally by treating $Mn(NO_3)_2$ and H_2L in a mixed solvent of DMF and water at 100 °C.[†] Note that product **1** was highly reproducible for repeated synthesis under the reaction conditions employed in this work. Compound **1** is insoluble in water and common organic solvents. It is formulated as $[Mn_2L_2(H_2O)_2\cdot 2DMF\cdot 2H_2O]_n$ based on IR, TG, elemental analysis and X-ray analysis data. Single crystal X-ray analysis[‡] revealed that compound **1** crystallized in monoclinic crystal system $P2_1/n$. As shown in Figure 1, the asymmetric unit consists of two Mn^{II} cations, two L^{2-} ligands, two coordinated water molecules, two free DMF molecules and two free water molecules. The four oxygen atoms of the L^{2-} anions adopt two coordination modes: one carboxyl group adopts a chelating coordination mode to bridge two Mn centers; the other carboxylate group coordinates to two Mn centers by

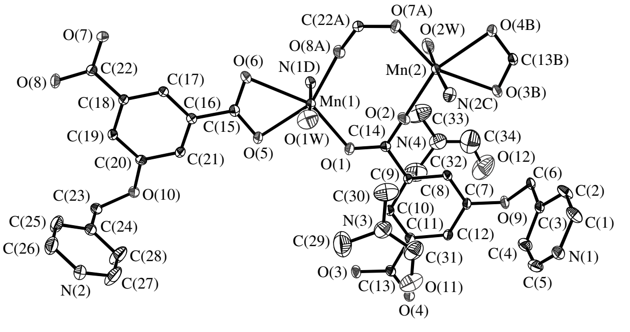


Figure 1 Molecular structure of complex **1** (probability of ellipsoid is 30%, all hydrogen atoms are omitted for clarity). Symmetry codes: A ($1.5-x$, $-0.5+y$, $-0.5-z$); B ($1.5-x$, $-0.5+y$, $0.5-z$); C ($2-x$, $2-y$, $-z$); D ($-0.5+x$, $1.5-y$, $0.5+z$). Selected bond lengths (nm): Mn(1)–O(1) 2.1282(18), Mn(1)–O(1W) 2.179(2), Mn(1)–O(8A) 2.0835(18), Mn(1)–N(1D) 2.268(2), Mn(2)–O(2W) 2.0746(18), Mn(2)–O(3B) 2.2876(18), Mn(2)–O(4B) 2.2583(17), Mn(2)–N(2C) 2.319(2).

[†] Reagents and solvents employed were commercially available and used as received.

General procedure for the preparation of complex **1**. A mixture of $Mn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol) and H_2L[12] (17.2 mg, 0.1 mmol) was added to 8 ml of DMF/H_2O (1:3, v/v) and adjusted to pH 6.0–7.0 with 1 M NaOH. The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 ml) under autogenous pressure and heated at 100 °C for three days; colorless crystals were obtained (yield 65% based on Mn). IR (KBr, ν/cm^{-1}): 3437 (s), 1657 (s), 1617 (m), 1584 (m), 1548 (s), 1448 (m), 1413 (m), 1377 (s), 1277 (w), 1246 (w), 1127 (w), 1102 (w), 1052 (m), 924 (w), 784 (m), 720 (m), 668 (m), 633 (w), 572 (w), 482 (w), 421 (w). Found (%): C, 48.12; H, 4.67; N, 6.52. Calc. for $C_{34}H_{36}Mn_2N_4O_{14}$ (%): C, 48.93; H, 4.35; N, 6.71.

adopting a monodentate coordination mode. Each Mn^{II} ion is six-coordinated by four oxygen atoms from two L^{2-} ligands, one oxygen atom from water and one nitrogen atom from one L^{2-} ligand, generating a distorted octahedral coordination geometry. In the octahedral, four oxygen atoms from two L^{2-} ligands locate at the equatorial plane, one oxygen atom from water molecule and one nitrogen atom from one L^{2-} ligand occupy the axial position. The bond angles O(8A)–Mn(1)–O(1), O(8A)–Mn(1)–O(6), O(1)–Mn(1)–O(5) and O(5)–Mn(1)–O(6) are 113.11(8)°, 94.53(8)°, 95.81(8)° and 89.07(11)°, respectively. The sum of these angles is 360.00°, suggesting a planar nature of four oxygen atoms from two L^{2-} ligands. The Mn–O distances range from 2.0835(18) to 2.4036(19) Å. The Mn–O and Mn–N bond lengths for the complex are comparable to that found in similar types of Mn^{II} octahedral complexes.[14,15] In compound **1**, the two Mn^{II} atoms are bridged by carboxylate oxygen atoms to form a binuclear cluster with a Mn(1)···Mn(2) separation of 4.434(5) Å. Each binuclear cluster is connected by O atoms to form a 2D net structure [Figure 2(*a*)], further generate 3D structure through the N atoms of pyridine ring from L^{2-} ligands [Figure 2(*b*)]. The two carboxylate groups of the H_2L ligand were deprotonated and coordinated with Mn.

A better insight into the nature of this intricate framework can be achieved by the application of a topological approach, reducing multidimensional structures to simple node and connection nets. Since the Mn atom is located in a symmetrical position, the $[Mn_2(CO_2)_4]$ secondary building unit can be regarded as one kind of nodes with the L^{2-} ligands considered as another linker. Thus, it is necessary to note that binuclear Mn-containing units can be regarded as six-connected nodes, and the L^{2-} ligand acts as three-connected nodes. Therefore, as determined by the TOPOS software,[16] the topology for this 3D network can be described as a $\{4^2.6\}_2\{4^4.6^2.8^7.10^2\}$ net [Figure 2(*c*)].

In addition, the IR spectra of complex **1** exhibit a strong wide band at 3437 cm^{-1} from ν_{O-H} of water molecules, and the asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching bands fall in the region of 1657–1377 cm^{-1}. The presence of the characteristic bands around 1657 cm^{-1} in the title complex was attributed to the full protonated carboxylic group of H_2L ligand. The separation ($\Delta\nu$) between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is 280 cm^{-1} for the complex, which is more than 200 cm^{-1}, indicating monodentate coordinating modes.[17] The absorption bands in the ranges of 1400–1600 and 1454–1348 cm^{-1} show the skeletal vibrations of the aromatic ring for the asymmetric and symmetric vibrations, respectively. In addition, X-ray diffraction analysis indicated the existence of the protonation of H_2L ligand. Therefore, the IR results are coincident with the crystallographic structural analysis data.

To estimate the stability of compound **1**, its thermal behavior was studied by TGA in a flow of N_2, in a temperature range from 20 to 700 °C (Figure 3) with a heating rate of 10 K min^{-1}. The TGA curve indicates that compound **1** starts to lose four coordination water molecules and ends at about 224 °C (the weight is 92.41%, the calculated value is 92.68%). After the loss of all the water molecules, the supramolecular framework is stable up to 389 °C, followed by another weight loss at a high temperature. The thermal decomposition feature of the complex is in good agreement with its crystal structure.

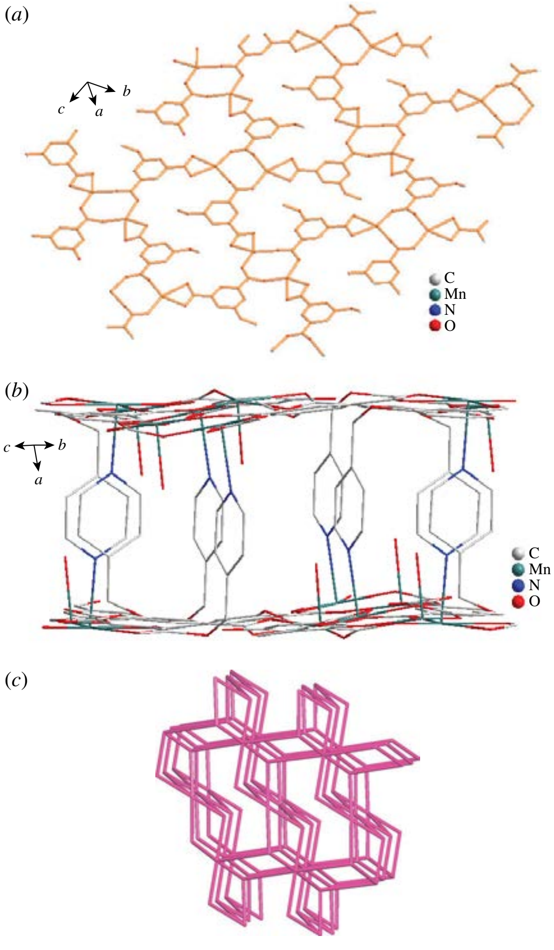


Figure 2 Views of the (*a*) 2D network of **1**, (*b*) 3D framework of **1** and (*c*) schematic view of the 3D topology of **1**.

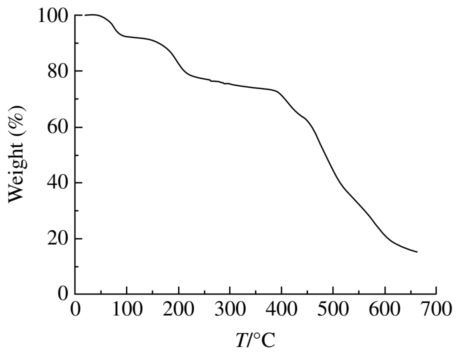


Figure 3 TG curve of complex **1**.

To confirm whether the crystal structure is truly representative of the bulk materials, an XRD experiment was carried out for **1**. The experimental and simulated XRD patterns of the complex are shown in Figure 4, which demonstrates that the bulk synthesized materials and the measured single crystal are the same.

The frameworks of Mn^{II} centers provide a good opportunity for investigating an effective magnetic property through carboxylate oxygen bridges.[18–21] The temperature dependence of magnetic susceptibility data for **1** is shown in Figure 5 in the form of $1/\chi_M$ and $\chi_M T$ *vs.* T plots. At room temperature, $\chi_M T$ is 8.95 cm^3 mol^{-1} K,

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‡ *Crystallographic data for complex* **1**. $C_{34}H_{36}Mn_2N_4O_{14}$, M_r = 834.55, monoclinic, space group $P2_1/n$, a = 14.4863(10), b = 15.9733(11) and c = 16.5214(12) Å, V = 3.7511(5) nm^3, Z = 4, d_{calc} = 1.478 g cm^{-3}, μ = = 0.745 mm^{-1}, F(000) = 1720.0, the final R = 0.0484, wR = 0.1216 and S = 1.032 for 9302 observed reflections with $I > 2\sigma(I)$. The measurements were performed on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[13] Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.

CCDC 1427921 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

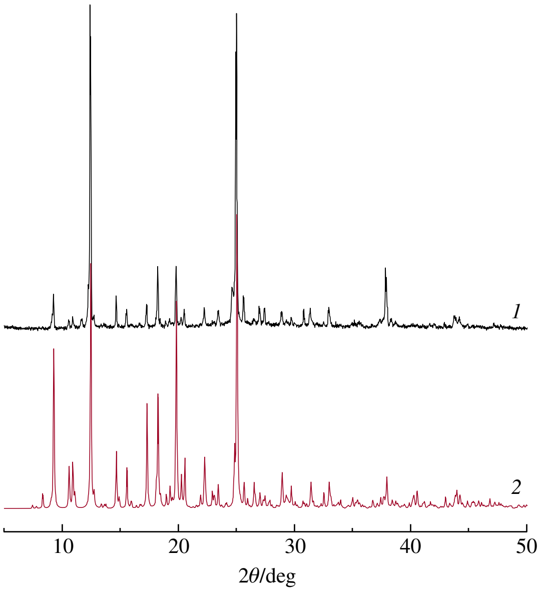

Figure 4 (*1*) Experimental and (*2*) simulated XRD spectra of complex **1**.

which is close to the expected value of 8.75 cm^3 mol^{-1} K for two isolated high-spin Mn^{II} ions ($g = 2$ and $S = 5/2$). Upon cooling, $\chi_M T$ rapidly decreases and is 1.19 cm^3 mol^{-1} K at $T = 2$ K. This feature reveals an overall antiferromagnetic behavior. From a magnetic viewpoint, it can be seen that the overall antiferromagnetic interaction should be mainly ascribed to carboxylate oxygen bridges. The magnetic properties of **1** also obey the Curie–Weiss law and give $C = 9.12$ cm^3 mol^{-1} K and $\theta = -9.08$ K. The negative values of θ indicate significant antiferromagnetic interactions between neighboring Mn^{II} ions. While, separations were bridged through the long spacer (a pyridine ring from L^{2-} ligand), it should exclude an efficient direct exchange between Mn^{II} centers; therefore, the overall antiferromagnetic interaction should be mainly attributed to the carboxylate oxygen bridge in binuclear Mn for **1**.

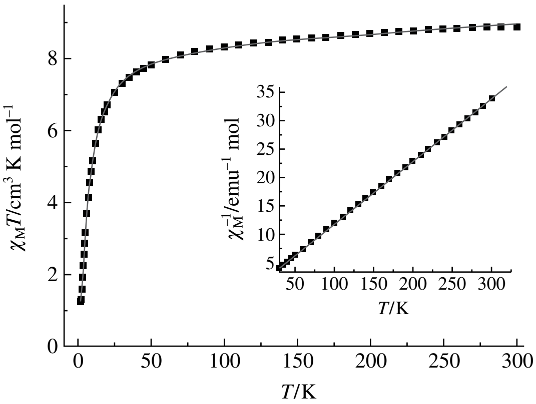

Figure 5 Temperature dependence of magnetic susceptibility in the form of $\chi_M T$ and $1/\chi_M$ (inset) for compound **1**. The line shows the best-fit curve to the Curie–Weiss fit law.

In summary, a novel 3D Mn coordination polymer has been synthesized by the self-assembly of a Mn salt with L^{2-} under hydrothermal conditions. The elemental analysis, IR, TG and single-crystal X-ray diffraction studies of the complex were performed, whose results agreed well with its structure. Magnetic susceptibility measurements revealed antiferromagnetic interaction between the adjacent Mn^{II} ions in the complex. Thus, it may provide a useful strategy for synthesizing a new magnetic coordination material.

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