

Synthesis, Crystal Structure, and Magnetic Properties of a New Manganese(II) Complex Based on 5-Bromoisophthalate and 1,2-Bis(4-pyridyl)-ethane Ligands

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A new Mn(II) complex, $[Mn(5-Br-ip)(bpa)]_n$ $[5-Br-H_2ip = 5-bromoisophthalate; bpa = 1,2-bis(4-pyridyl)-ethane], has been prepared by hydrothermal reactions of Mn(II) salt and 5-bromoisophthalic acid with bpa and characterized by elemental analysis and single crystal x-ray analysis. The title complex belongs to the monoclinic system,$ *P2/c*space group, <math>a = 10.2935(7) Å, b = 13.7759(10) Å, c = 17.0594(12) Å, $\beta = 103.9340(10)^\circ$, F(000) = 964. R₁ = 0.0586, wR₂ = 0.1716. Complex 1 consists of a two-dimensional (2D) network containing noncentrosymmetric dinuclear Mn units as nodes, and further extends into a three-dimensional (3D) supramolecular architecture via weak interlayer Br...Br interactions. Moreover, the magnetic property of the title complex was investigated.

Keywords 5-bromoisophthalate, crystal structure, hydrothermal synthesis, magnetic property

INTRODUCTION

The construction of metal-organic frameworks (MOFs) has become an exciting and expanding approach to novel materials. The interest is stimulated not only by the MOFs' structural diversities but also by their extensive potential applications in such areas as separation, molecular recognition, ion exchange, gas sorption and storage, nonlinear optics, magnetics, and catalysis.^[1–7] In principle, the most effective approach for the construction of MOFs is to rationally modify the building blocks and to control the assembled motifs for required products via selecting different organic ligands.^[8,9] Among the various ligands, isophthalic acid (H₂isop) and its derivatives with special conformations, such as with a 120° angle between two carboxylic groups, have been extensively used to prepare a variety of coor-

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dination polymers in virtue of the robust and versatile coordination capability of carboxylate.^[8–14] However, the related dicarboxylate ligands bearing noncoordinated electron-withdrawing and electron-donating groups on the aromatic backbone have received less attention at this stage. 5-Bromoisophthalate (5-Br-H₂ip), may serve as a suitable building block to construct novel coordination polymers, due to the existence of a noncoordinating electron-withdrawing Br group on the aromatic backbone, which will have a profound impact on the electron density of such a ligand and therefore different physical and chemical properties.^[15–18] Here we report the synthesis and crystal structure of a new complex, [Mn(5-Br-ip)(bpa)]_n. Moreover, the magnetic property of this complex was investigated.

EXPERIMENTAL

Materials and Physical Measurements

All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The crystal determination was performed on a Bruker Smart Apex II CCD diffractometer equipped with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). The magnetic measurement was performed on the Quantum Design Squid MPMS XL-7 instrument in the temperature range of 2–300 K.

Synthesis of [Mn(5-Br-ip)(bpa)]_n

This complex was prepared under hydrothermal conditions. A mixture of 5-Br-H₂ip (0.2 mmol), bpa (0.2 mmol), Mn(OAc)₂·4H₂O (0.2 mmol), KOH (5.6 mg, 0.2 mmol), and H₂O (16 mL) was placed in a Teflon-lined stainless-steel vessel, heated to 140°C for 72 h, and then cooled to room temperature over 36 h. Yellow block crystals of **1** were collected by filtration, washed with water, and dried in air. Anal.: Calcd. (%) for C₂₀H₁₅BrMnN₂O₄: C, 49.82; H, 3.14; N, 5.81. Found (%):C, 49.85; H, 3.08; N, 5.85.

Crystallographic Data Collection and Structure Determination

Single crystal x-ray diffraction analysis of **1** was carried out on a Bruker Smart Apex II CCD diffractometer equipped with

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Crystallographic data		
Empirical formula	$C_{20}H_{15}BrMnN_2O_4$	
Formula weight	482.19	
Temperature (K)	296(2)	
Crystal system	Monoclinic	
Space group	<i>P2/c</i>	
Unit cell dimensions	a = 10.2935(7) Å	
	b = 13.7759(10) Å	
	c = 17.0594(12) Å	
	$\beta = 103.9340(10)$ å	
Volume, Z	2347.9(3) Å ³ , 4	
$D_c ({\rm kg} {\rm m}^{-3})$	1.364	
<i>F</i> (000)	964	
Crystal size (mm ³)	$0.21 \times 0.18 \times 0.15$	
θ range for data collection (å)	2.46-25.49	
Reflections collected	17566	
Independent reflections	4375R(int) = 0.0194	
Final <i>R</i> indices $(I > 2\sigma(I))$	R = 0.0586, wR = 0.1716	
<i>R</i> indices (all data)	R = 0.0676, wR = 0.1792	

TABLE 1



FIG. 1. A perspective drawing of the Mn(II) environment.

graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by using the φ/ω scan technique at room temperature. The structure was solved by direct methods with SHELXS-97.^[19] Empirical absorption corrections were applied with the SADABS program.^[20] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F² was carried out using SHELXL-97.^[21] Table 1 shows crystallographic crystal data of **1**. Selected bond lengths and angles are listed in Table 2.

RESULTS AND DISCUSSION

Crystal Structure Description

$[Mn(5-Br-ip)(bpa)]_n$.

The structure of 1 consists of a two-dimensional (2D) network containing noncentrosymmetric dinuclea Mn units as

nodes. As depicted in Figure 1, the asymmetric unit of 1 contains one Mn(II) ion, one 5-Br-ip ligand, and one bpa ligand. Each octahedral Mn(II) ion is coordinated by four carboxylate oxygen atoms of three 5-Br-ip anions, located at the basal equatorial plane, and a pair of pyridyl nitrogen atoms of bpa from the axial positions with an N1-Mn(1)-N2A angle of 171.8(3)°. The Mn–O and Mn–N bond lengths are in the range of 2.113(3)-2.347(3) and 2.200(7)-2.332(5) Å, respectively, which are in the normal range expected for such coordination bonds.^[8,9] In this structure, the Mn…Mn distance in the [Mn₂(COO)₂] dimeric unit is 4.347(1) Å. Each 5-Br-ip anion serves as a tridentate ligand to link the Mn(II) centers to generate a one-dimensional (1D) polymeric motif (Figure 2). These 1D motifs are further connected by bpa ligands to form a 2D layer (Figure 3), which extends into a three-dimensional (3D) supramolecular architecture via weak interlayer Br...Br interactions (Br...Br distance: 3.5123(7) Å). From the topological

TABLE 2	
Selected bond lengths (Å) and bond angles (⁾

Mn(1)–O(2)#2	2.113 (3)	O(1)–Mn(1)–N(1)	85.91 (13)
Mn(1)–O(1)	2.136 (3)	O(3)#4-Mn(1)-N(1)	92.65 (14)
Mn(1)–O(3)#4	2.202 (3)	O(2)#2-Mn(1)-N(2)#3	91.9 (3)
Mn(1)–O(4)#4	2.347 (3)	O(2)#2-Mn(1)-O(3)#4	92.25 (12)
Mn(1)-N(1)	2.275 (4)	O(2)#2-Mn(1)-N(1)	94.08 (14)
Mn(1)–N(2)#3	2.332 (5)	O(1)-Mn(1)-N(1)	85.91 (13)
O(2)#2–Mn(1)–O(3)#4	92.25 (12)	O(3)#4-Mn(1)-N(1)	92.65 (14)
O(2)#2-Mn(1)-N(1)	94.08 (14)	O(2)#2-Mn(1)-N(2)#3	91.9 (3)

Symmetry transformations used to generate the equivalent atoms: #2, -x + 1, y, -z + 3/2; #3, x, y - 1, z; #4, x - 1, y, z.



FIG. 2. A view of the 1D chain structure.

view, if each Mn1 ion is considered as a five-connected node, and 5-bromoisophthalic acid anion acts as a three-connected node, the structure of **1** can be considered as a (3,5)-connected network with a Schläfli symbol of $(4^2 \cdot 6)(4^2 \cdot 6^7 \cdot 8)$ (Figure 4).

Magnetic Property

From the magnetic point of view, complex **1** can be considered as dinuclear, in which two Mn(II) ions are linked by two carboxylate bridges, since coupling through 5-bromoisophthalic acid and bpa is almost negligible. The magnetic susceptibilities

of **1** were measured in the 2–300 K temperature range, and are shown as $\chi_M T$ and χ_M versus T plots in Figure 5. The experimental $\chi_M T$ value of **1** at room temperature is 8.53 cm³ K mol⁻¹, which is close to that expected for a non-interacting pair of S = 5/2 ions (8.75 cm³ K mol⁻¹, S = 5/2) of the Mn(II). As temperature is lowered to 2 K, the $\chi_M T$ values decrease, first slowly and then rapidly. The behavior suggests that anti-ferromagnetic interactions are operative in **1**.

In order to quantitatively evaluate these magnetic interactions, for similar binuclear Mn(II) complexes, the following



FIG. 3. A view of the 2D layer structure.



FIG. 4. Schematic representation of the (3,5)-connected $(4^2 \cdot 6)(4^2 \cdot 6^7 \cdot 8)$ topology.

equation is induced from the Hamiltonian $\hat{H} = -JS_1S_2^{[22]}$:

$$\chi_{M} = 2 \frac{Ng^{2}\beta^{2}}{KT} \frac{A}{B}$$
[1]

$$A = \exp[2J/KT] + 5 \exp[6J/KT] + 14 \exp[12J/KT] + 30 \exp[20J/KT] + 55 \exp[30J/KT]$$

$$B = 1 + 3 \exp[2J/KT] + 5 \exp[6J/KT] + 7 \exp[12J/KT] + 9 \exp[20J/KT] + 11 \exp[30J/KT]$$



FIG. 5. Temperature dependence of $\chi_M T$ and χ_M for 1. Open points are the experimental data, and the solid line represents the best fit obtained from the Hamiltonian given in the text.

The least-squares analysis of magnetic susceptibilities data led to J = -1.32 cm⁻¹, g = 2.04, and $R = 4.56 \times 10^{-4}$ for **1**. The J values suggest that weak anti-ferromagnetic interactions between the neighboring Mn(II) ions are mediated through carboxylate bridges.

CONCLUSIONS

In summary, we have prepared a new 5-bromoisophthalate complex with Mn(II) salt with 1,2-bis(4-pyridyl)-ethane as the ancillary ligand. Compound **1** is a 2D network containing non-centrosymmetric dinuclear Mn units as nodes and further extends into a 3D supramolecular architecture via weak interlayer Br...Br interactions. The magnetic property of the complex was also investigated. Further systematic studies for the design and synthesis of such polymers with noncoordinated electron-withdrawing and electron-donating groups are underway in our laboratory.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 780632. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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