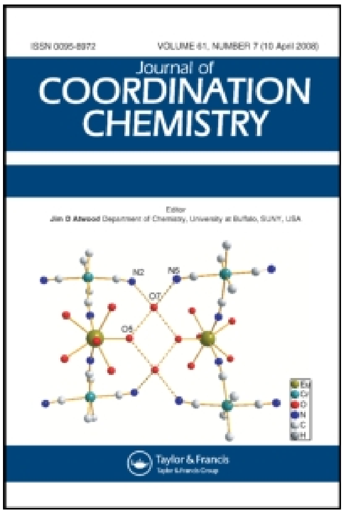

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Synthesis, crystal structure and magnetic property of a three-dimensional manganese(II) complex

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The solvothermal reaction of $MnCl_2 \cdot 4H_2O$, H_2asp and CH_3ONa gave rise to a new manganese(II) complex, $\{[Mn(asp)(H_2O)] \cdot (H_2O)_2\}_n$ (**1**) ($H_2asp = $ 5-aminoisophthalic acid). Single-crystal X-ray diffraction analysis reveals that complex **1** is a three-dimensional consisting of two-dimensional layers extended by hydrogen bonding interactions. The two-dimensional layer contains 8-, 14-, and 16-membered rings. A variable temperature magnetic measurement of **1** displays weak antiferromagnetic behavior.

Keywords: Manganese(II); Solvothermal reaction; X-ray diffraction; Magnetic properties

1. Introduction

The crystal engineering of coordination frameworks and supramolecular assemblies is a current area within inorganic chemistry. This not only stems from their intriguing architectures and new topologies, but also from their potential application in functional materials, nanotechnology and biological recognition [1, 2]. The architectures and properties mainly depend on the nature of metal centers and the organic ligands used [3–5]. For magnetic properties, besides the effect of different coupling paramagnetic metal ions and their specific coordination preferences, the choice of appropriate bridging ligands with functional groups and suitable spacers is also critical [6–10]. Carboxylates provide efficient superexchange pathways between paramagnetic metal ions and can adopt various coordination conformations. Many metal-carboxylate frameworks with ferromagnetic, antiferromagnetic and metamagnetic behavior have been successfully prepared [11–13]. In the course of constructing extended structural motifs, either di- and multi-carboxylate ligands, or multifunctional carboxylate-containing ligands incorporating other coordination groups have been employed [14–17].

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N or S donor atoms coordinating to metal centers can result in fascinating high-dimensional complexes with beautiful aesthetics and useful functional properties, which cannot be obtained from carboxylate ligands alone [18, 19]. The deprotonated 1,3,5-benzenetricarboxylic acid (btc) as a three-connector ligand has been widely applied in the construction of high-dimensional porous materials [20, 21]. 5-Aminoisophthalic acid (H_2asp) possessing one amino group and two carboxylate groups, can be considered as one carboxylate group in btc is replaced by an amino group. However, the amino group can also coordinate to transition metal ions, as manifested in some compounds [22–25]. Hence, 5-aminoisophthalic acid can be expected to be an analogue of 1,3,5-benzenetricarboxylic acid, as a starting material to formulate novel extended polymeric networks. Herein, we report the synthesis and crystal structure of a three-dimensional supramolecular framework $\{[Mn(asp)(H_2O)]\cdot(H_2O)_2\}_n$ (H_2asp = 5-Aminoisophthalic acid) (**1**), which is constructed from the two-dimensional layers containing 8-, 14-, and 16-membered rings extended by abundant hydrogen bonding interactions. The magnetic properties of **1** show weak antiferromagnetic behavior.

2. Experimental

2.1. *Materials and physical measures*

5-Aminoisophthalic acid was purchased from Aldrich and used without further purification; all the other reagents were commercially available and used as purchased. An IR spectrum as a KBr disk was recorded on a Magna 750 FT–IR spectrophotometer. Elemental analyses were carried out in the elemental analysis group of this institute on an Elementary Vario ELIII analyzer. Temperature-dependent magnetic-susceptibility measurements on powdered solid samples were performed on a Quantum Design PPMS-9T magnetometer in the temperature range 2 ~300 K. The magnetic field applied was 5 kOe. The observed susceptibility data were corrected for underlying diamagnetism by using Pascal's constants [26].

2.1.1. $\{[Mn(asp)(H_2O)]\cdot(H_2O)_2\}_n$ (1). $MnCl_2\cdot4H_2O$ (0.25 mmol, 0.049 g) and H_2O (10 mL) were placed in a Teflon-lined stainless steel vessel, then H_2asp (0.25 mmol, 0.045 g) and CH_3ONa (0.50 mmol, 0.027 g) in CH_3OH (8 mL) were added. The mixture was sealed and heated to 170°C for 96 hours, then cooled to room temperature over 24 hours. Yellow block crystals were obtained. Yield: 42% (based on Mn). Elemental analysis (%): Calcd for $C_8H_{11}MnNO_7$ (288.12): C 33.35, H 3.85, N 4.86; found: C 33.33, H 3.76, N 4.92. IR (KBr, cm^{-1}): 3443 (br), 1610 (m), 1571 (vs), 1528 (m), 1388 (vs), 1014 (w), 984 (w), 944 (m), 785 (s), 730 (s), 676 (m), 575 (w), 536 (w).

2.2. *Crystallographic data and structure determination*

Measurement of **1** was conducted on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at low temperature (−100°C) [27]. The structure was solved by direct methods [28] and refined on F^2 by full-matrix least-squares using the SHELXL-97 program package [29]. The positions of H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic

Table 1. Crystal data and structure determination summary for complex **1**.

Formula	$C_8H_{11}MnNO_7$
Formula weight	288.12
Crystal size (mm^3)	0.20 × 0.20 × 0.20
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.7255(15)
b (Å)	8.5693(17)
c (Å)	8.6765(17)
α (°)	85.07(3)
β (°)	76.20(3)
γ (°)	66.30(3)
V (Å^3)	510.74(17)
Z	2
D_c ($g\,cm^{-3}$)	1.873
μ (mm^{-1})	1.318
T (K)	173(2)
λ(Mo-Kα) (Å)	0.71073
Reflections collected	3926
Unique reflections	2299
R_{int}	0.0119
Parameters	186
S on F^2	1.030
R_1 ($I > 2\sigma(I)$)^a	0.0222
WR_2 ($I > 2\sigma(I)$)^b	0.0598
R_1 (all data)	0.0242
WR_2 (all data)^b	0.0613
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ [e Å^{-3}]	0.401 and −0.239

$^a R = \sum \|F_o| - |F_c\| / \sum |F_o|$. $^b WR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Crystal data and structure determination summaries for **1** are listed in table 1, selected bond distances and angles in table 2.

3. Results and discussion

3.1. *Description of the crystal structure*

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$ and is a three-dimensional supramolecular architecture built from two-dimensional layers extended by hydrogen bonding interactions. This structure is distinctly different from manganese(II)-btc structures because of the different structural conformations and different coordination modes between amino and carboxylate groups [30, 31]. Selected bond distances and angles are given in table 2. As shown in figure 1, Mn^{II} is in a distorted octahedral geometry. The equatorial basal plane is determined by one coordinated water molecule with the bond length of Mn–OW1 being 2.1484(12) Å and three carboxylate oxygen atoms from two different asp ligands. The deviation of the Mn^{II} center from the mean plane is 0.0944 Å. The axial positions are occupied by one carboxylate oxygen atom and *one* amino nitrogen atom from different

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

Mn–O1A	2.2405(11)	Mn–O3B	2.1346(12)
Mn–O2A	2.3388(13)	Mn–O4C	2.1138(14)
Mn–OW1	2.1484(12)	Mn–N	2.3595(14)
O4C–Mn–O3B	100.03(5)	OW1–Mn–O2A	90.55(5)
O4C–Mn–OW1	122.21(5)	O1A–Mn–O2A	57.41(4)
O3B–Mn–OW1	89.69(5)	O4C–Mn–N	85.39(5)
O4C–Mn–O1A	89.61(4)	O3B–Mn–N	173.47(4)
O3B–Mn–O1A	88.82(4)	OW1–Mn–N	84.31(5)
OW1–Mn–O1A	147.87(4)	O1A–Mn–N	94.89(5)
O4C–Mn–O2A	144.98(4)	O2A–Mn–N	86.10(5)
O3B–Mn–O2A	91.41(5)		

Symmetry codes: A: $-x, -y, -z+2$; B: $x-1, y+1, z$; C: $-x+1, -y, -z+1$.

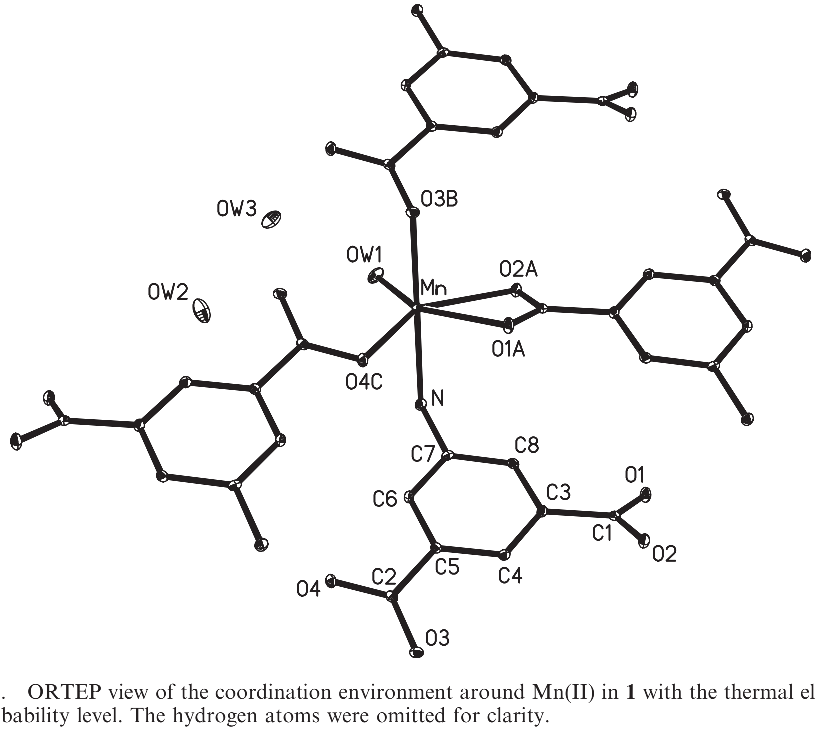
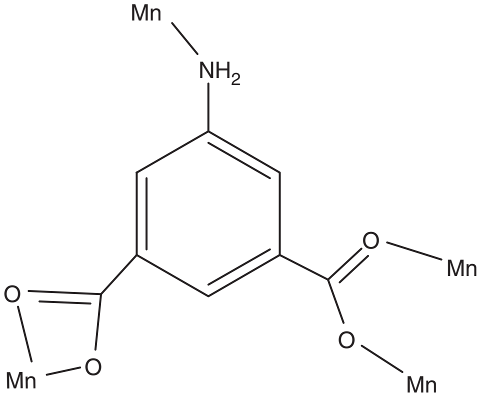


Figure 1. ORTEP view of the coordination environment around Mn(II) in **1** with the thermal ellipsoids at 30% probability level. The hydrogen atoms were omitted for clarity.

asp ligands. The bond length of Mn–N is 2.3595(14) Å, which is shorter than that reported by Hong's group [32], the bond angle of O3B–Mn–N is 173.47(4)°. The Mn–O(carboxylate) bond distances are in agreement with those observed in other manganese(II)–carboxylate complexes [30, 31, 33]. Each asp bridges four $\mathrm{Mn^{II}}$ centers through its amino group, one chelating and one bridging carboxylate groups, (scheme 1). Thus, asp links $\mathrm{Mn^{II}}$ centers along different directions into a two-dimensional layer, with different macrocyclic rings (8-, 14- and 16-membered rings) (figure 2). The two-dimensional layer is further extended into a three-dimensional supramolecular architecture through abundant hydrogen bonding interactions involving coordinated water molecules and carboxylate groups [$\mathrm{OW1{-}H\cdots O2^{i}}$ 2.704 Å, symmetry codes: (i) x, $y+1$, z], free water molecules and carboxylate groups



Scheme 1. Coordination mode of asp.

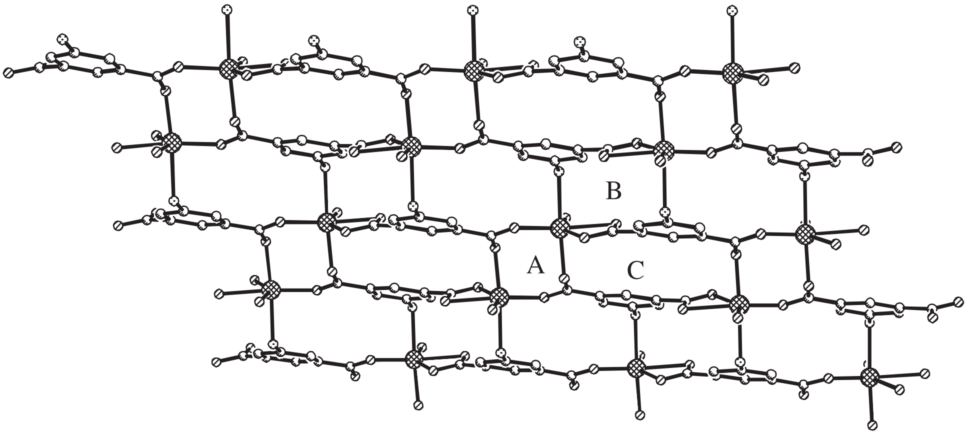


Figure 2. A two-dimensional layer containing 8-, 14- and 16-membered rings in **1** (A = 8-, B = 14-, C = 16-membered ring, respectively).

[OW2–H $\cdots$ $O3^{ii}$ 2.830 Å, OW(3)–H $\cdots$ $O1^{iii}$ 2.810 Å, symmetry codes: (ii) $-x$, $-y$, $1-z$; (iii) $-x$, $1-y$, $2-z$], coordinated water molecules and free water molecules [OW1–H $\cdots$ OW3, 2.744 Å], free water molecules and free water molecules [OW2–H $\cdots$ $OW2^{iv}$, 2.889 Å; OW2–H $\cdots$ OW3, 2.829 Å; OW3–H $\cdots$ $OW3^{v}$ 2.828 Å, symmetry codes: (iv) $1-x$, $1-y$, $1-z$; (v) $-x$, $2-y$, $1-z$] (figure 3).

3.2. *Magnetic properties*

The temperature-dependent magnetic susceptibility of complex **1** was measured in the 2–300 K temperature range and is shown in figure 4. χ_m increases quickly on cooling, from 0.027 $cm^3 mol^{-1}$ at 300 K to the maximum of 0.373 $cm^3 mol^{-1}$ at 6.6 K, after which it decreases to 0.332 $cm^3 mol^{-1}$ at 2 K. At 300 K, the μ_{eff} value is 8.10 B.M., slightly lower than the expected value of 8.37 $cm^3 mol^{-1} K$ for four magnetically isolated high spin Mn(II) ions ($S_{Mn} = 5/2$, $g = 2.0$). The overall behavior of **1** indicates

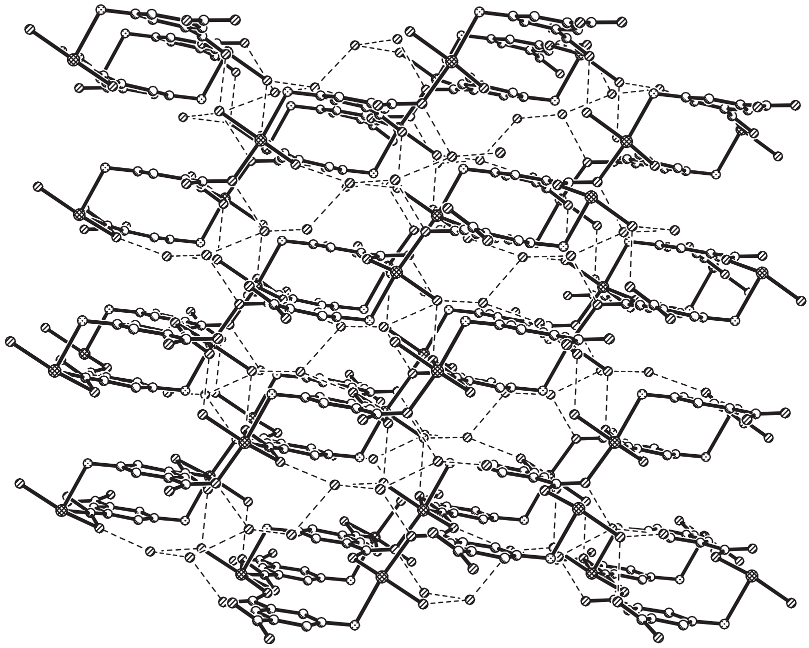


Figure 3. A three-dimensional supramolecular framework constructed from two-dimensional layer extended by hydrogen bonding interactions.

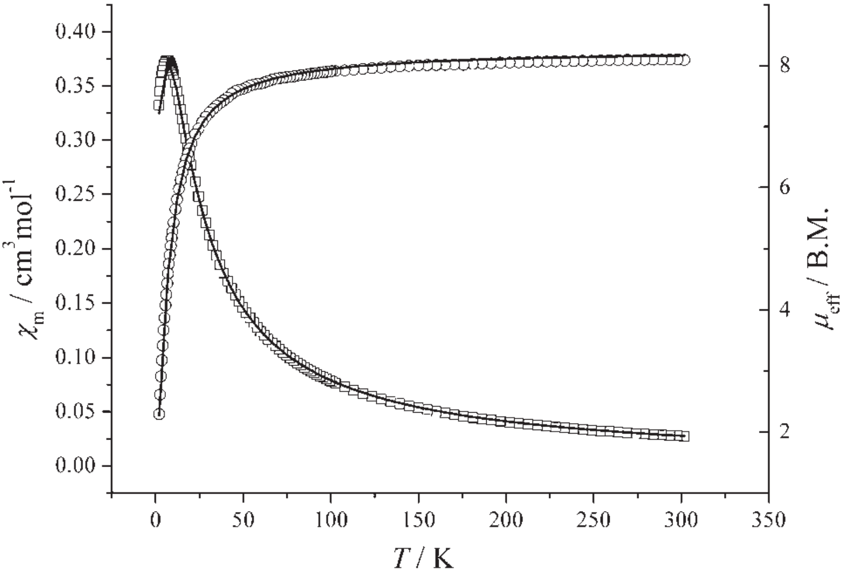


Figure 4. Experimental molar susceptibility (□) and effective magnetic moment (○) of temperature dependence for complex **1**. The solid line represents the calculated values.

a dominant weak antiferromagnetic coupling. According to its structure, the fitting of the magnetic data of **1** was performed based on a dimer (J) with treatment of the molecular field approximation (zJ'). Corresponding magnetic susceptibility is represented by using the spin–spin coupling Hamiltonian appropriate for describing the magnetic exchange interaction of the dinuclear Mn(II) unit.

$$\hat{H} = -J\hat{S}_1\hat{S}_2$$
$$\chi_{bi} = \frac{2Ng^2\beta^2}{kT}\left[\frac{A}{B}\right] \tag{1}$$

$$A = 55 + 30\exp(-5J/kT) + 14\exp(-9J/kT) + 5\exp(-12J/kT) + \exp(-14J/kT)$$
$$B = 11 + 9\exp(-5J/kT) + 7\exp(-9J/kT) + 5\exp(-12J/kT) + 3\exp(-14J/kT) + \exp(-15J/kT)$$

$$\chi_\mathrm{m} = \frac{\chi_{bi}}{(1 - 2zJ'\chi_{bi}/Ng^2\beta^2)} \tag{2}$$

The molecular field approximation [34] was used to treat the interaction between the dinuclear Mn(II) units, giving the susceptibilities of the system. The least-square fitting of the experimental data leads to $g = 1.98$, $J = -1.14\,\mathrm{cm}^{-1}$, $zJ' = -0.08\,\mathrm{cm}^{-1}$, and $R = 1.497 \times 10^{-6}$. This fitting supports the magnetic exchange interaction passing through the double μ-carboxylate bridge, thus exhibiting antiferromagnetic exchange.

4. Conclusion

In summary, a three-dimensional supramolecular network containing 8-, 14-, and 16-membered rings has been generated from the solvothermal reaction of $MnCl_2 \cdot 4H_2O$, 5-aminoisophthalic acid and CH_3ONa. A variable temperature magnetic study (2–300 K) indicates a weak antiferromagnetic interaction.

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC number 266580).

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