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Syntheses, crystal structures and magnetic behaviors of three Mn^{II}-terephthalate coordination polymers containing terminal ligands

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ABSTRACT

Three Mn^{II} -terephthalate coordination polymers, $\{Mn^{II}(tp)(bpy)(H_2O)\}_n$ (1), $\{Mn^{II}_3(tp)_{6/2}(bpy)_2 \cdot (dmf)\}_n$ (2) and $\{Mn^{II}(tp)(phen)\}_n$ (3) (tp = terephthalic dianion, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) have been synthesized and characterized by single crystal X-ray diffraction studies and low temperature (2–300 K) magnetic measurements. The structure analysis of 1–3 show that they all are coordination polymers composed of Mn atoms as nodes and terephthalate dianions as spacers. Interestingly, compound 1 consists of 1D infinite zigzag chains, while compound 2 consists of 2D sheets and compound 3 has a 3D framework structure. The study of the temperature dependent magnetic susceptibilities revealed that all of the polymers show antiferromagnetism.

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1. Introduction

The design and construction of multi-dimensional functional metal-organic coordination polymers with metal ions as nodes and bridging ligands as spacers have attracted much attention from chemists in recent years [1–3]. This has arisen not only for their various intriguing topological structures, but also for their unexpected properties for potential practical applications in material chemistry, such as heterogeneous catalysis, gas sorption, storage and separations, molecular recognition, non-linear optics, luminescent and magnetic properties [4–6].

Selection of the appropriate multidentate ligand to link paramagnetic metal ions is a powerful way for the building of polyfunctional coordination polymers. As a multidentate ligand, terephthalic acid (H₂tp) and its dianion have been used in synthetic systems, not only because they can act as short bridges via one carboxylic group or long bridges via the benzene ring, leading to abundant varieties of multi-dimensional coordination polymers with various kinds of topology, but also terephthalic acid, as an example of a benzenedicarboxylic acid, has a rigid aromatic unit as a spacer which can make give rise to very special systems that can have interesting electronic and magnetic interactions between the metal ions in the network through possible conjugative interactions (shown in Scheme 1) [7,8].

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On the other hand, the terminal ligands play an important role in the structures and properties of the coordination polymers [9].

Herein, we report the synthesis, crystal structure and magnetic properties of three manganese coordination polymers, { $Mn^{II}(tp)-(bpy)(H_2O)$ }_{*n*} (1), { $Mn^{II}_{3}(tp)_{6/2}(bpy)_2 \cdot (dmf)$ }_{*n*} (2) and { $Mn^{II}(tp)-(phen)$ }_{*n*} (3) (tp = terephthalic dianion, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, dmf = *N*,*N*-dimethylformamide), with the terephthalic dianion acting as a bridging ligand and 2,2'-bipyridine (in 1 and 2) and 1,10-phenanthroline (in 3) as terminal ligands.

2. Experimental

2.1. Materials and general methods

All reagents for the syntheses and analyses were obtained commercially, were of analytical grade and were used without further purification, and all manipulations were carried out in the laboratory atmosphere. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded as KBr pellets on a Bruker EQUINOX 55 IR spectrometer. Magnetic measurements were carried out with polycrystalline samples on a Quantum Design MPMS XL-5 SQUID magnetometer. The diamagnetic corrections were evaluated from Pascal's constants.





2.2. Syntheses of complexes 1 and 3

2.2.1. $\{Mn^{ll}(tp)(bpy)(H_2O)\}_n$ (1)

A mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.169 g, 1 mmol) in water (10 ml) and terephthalic acid (0.166 g, 1 mmol) in NaOH (80 mg, 2 mmol) aqueous solution (10 ml) were stirred at room temperature for about 12 h. Yellow crystals of compound **1** were obtained by diffusion of a 10 ml ethanol solution of 2,2'-bipyridine (0.156 g, 1 mmol) and the filtrate of the mixed solution after about 1 week (yield: about 32% based on Mn). *Anal.* Calc. for {Mn^{II}(tp)(bpy)-(H₂O)}_n (**1**): C, 54.98; H, 3.59; N, 7.12. Found: C, 55.01; H, 3.62; N, 7.16%. IR (KBr, cm⁻¹): 1576.53 s, 1475.14 m, 1438.82 s, 1378.05 s, 1151.97 m, 1058.54 w, 1018.48 m, 866.10 w, 805.18 m, 760.16 s, 736.45 m, 649.63 m, 524.31 m.

2.2.2. { $Mn_{3}^{II}(tp)_{6/2}(bpy)_{2} \cdot (dmf)$ }_n (2)

A solution of $MnCl_2$ (0.136 g, 1 mmol) in 10 ml of water was added to a solution of terephthalic acid (0.249 g, 1.5 mmol) and 2,2'-bipyridine (0.156 g, 1 mmol) in DMF (10 ml), stirring for about 2 h at room temperature. Then the resulting solution was transferred into a Teflon-Steel autoclave inside a programmable electric furnace reactor. The mixed-solvo-thermal reaction lasted for about

Table 1

Crystallographic data and	l structure refinement summary	for complexes 1–3
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	-		
	1	2	3
Formula	C ₁₈ H ₁₄ MnN ₂ O ₅	C47H35Mn3N5O13	C ₂₀ H ₁₂ MnN ₂ O ₄
Mr	393.25	1042.62	399.26
Temperature (K)	290(2)	290(2)	290(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/n	C2/c	C2/c
a (Å)	9.8665(3)	18.4033(2)	17.4786(11)
b (Å)	16.3330(6)	25.7135(3)	10.3332(6)
c (Å)	11.3035(4)	9.90320(10)	9.3359(6)
β (°)	111.6760(10)	91.4350(10)	96.173(3)
V (Å ³)	1692.75(10)	4684.86(9)	1676.38(18)
Ζ	4	4	4
D_{calc} (g cm ⁻³)	1.543	1.478	1.582
Crystal size (mm)	$0.30 \times 0.24 \times 0.16$	$0.32 \times 0.24 \times 0.20$	$0.26 \times 0.24 \times 0.20$
Theta range (°)	2.31 to 28.33	2.21 to 28.28	2.29 to 28.28
Reflections collected/ unique	16733/4190	21921/5786	8019/2086
R _{int}	0.0292	0.0203	0.0274
Completeness to theta	99.5% (28.33)	99.5% (28.28)	99.6% (28.28)
Data/restraints/ parameters	4190/0/240	5786/0/325	2086/0/124
Refinement	full-matrix least-	full-matrix least-	full-matrix least-
method	squares on F^2	squares on F^2	squares on F^2
Goodness-of-fit on F ²	1.056	1.030	1.037
Final R_1 and wR_2	$R_1 = 0.0317$,	$R_1 = 0.0323$,	$R_1 = 0.0296$,
indices	$wR_2 = 0.0868$	$wR_2 = 0.0949$	$wR_2 = 0.0895$
R_1 and wR_2	$R_1 = 0.0468$,	$R_1 = 0.0398$,	$R_1 = 0.0379$,
indices (all data)	$wR_2 = 0.0918$	$wR_2 = 0.0991$	$wR_2 = 0.0924$
Min, Max peaks (e Å ⁻³)	0.321 and -0.244	0.504 and -0.431	0.308 and -0.261

Table 2

Selected bond lengths (Å) and angles (°) for complex 1

Mn(1)-O(1)	2.2709(11)	Mn(1)-N(1)	2.2615(14)
Mn(1)-O(2)	2.2854(11)	Mn(1)-N(2)	2.2391(14)
Mn(1)-O(3)#1	2.0985(11)	Mn(1)-O(5)	2.1625(12)
O(1) - Mn(1) - O(2)	57.30(4)	N(1)-Mn(1)-O(2)	95.66(5)
O(1)-Mn(1)-O(3)#1	97.98(5)	N(1)-Mn(1)-O(1)	94.23(5)
O(1) - Mn(1) - O(5)	146.97(5)	N(2)-Mn(1)-O(1)	88.78(5)
O(3)#1-Mn(1)-O(2)	105.69(5)	N(2)-Mn(1)-O(2)	143.80(5)
O(3)#1-Mn(1)-O(5)	86.90(5)	N(2)-Mn(1)-N(1)	72.73(5)
O(3)#1-Mn(1)-N(2)	90.01(5)	O(5)-Mn(1)-O(2)	89.86(5)
O(3)#1-Mn(1)-N(1)	158.63(5)	O(5)-Mn(1)-N(1)	92.37(5)
O(5)-Mn(1)-N(2)	124.01(5)		

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

Table 3 Selected bond lengths (Å) and angles (°) for complex 2

Mn(1)-O(2)	2.1323(11)	O(1)-C(11)	1.266(2)
Mn(1)-O(4)	2.2104(10)	O(2)-C(11)	1.240(2)
Mn(1)-O(6)	2.1094(12)	O(4)-C(15)	1.288(2)
Mn(2)-O(1)	2.1162(11)	O(3)-C(15)	1.242(2)
Mn(2)-O(4)	2.2057(11)	O(5)-C(19)	1.257(2)
Mn(2)-O(5)	2.0912(11)	C(19)-O(6)	1.243(2)
Mn(2)–N(1)	2.2534(14)	C(23)-O(7)	1.73(3)
Mn(2) - N(2)	2.2959(15)	O(4)-Mn(2)-N(2)	87.53(5)
O(2)#1-Mn(1)-O(2)	180.00(5)	N(1)-Mn(2)-N(2)	71.70(5)
O(4)-Mn(1)-O(4)#1	180.0	C(1)-N(1)-Mn(2)	123.09(12)
O(6)#1-Mn(1)-O(6)	180.00(6)	C(5)-N(1)-Mn(2)	118.52(12)
O(6) - Mn(1) - O(2)	93.64(6)	C(19)-O(5)-Mn(2)	121.26(10)
O(2) - Mn(1) - O(4)	88.08(4)	C(10)-N(2)-Mn(2)	123.69(13)
O(6) - Mn(1) - O(4)	89.58(5)	C(6)-N(2)-Mn(2)	117.11(12)
O(5)-Mn(2)-O(1)	101.82(5)	C(11)-O(1)-Mn(2)	126.39(10)
O(5)-Mn(2)-O(4)	109.14(4)	C(11)-O(2)-Mn(1)	140.47(12)
O(1)-Mn(2)-O(4)	93.89(4)	O(2)-C(11)-O(1)	125.66(15)
C(19) - O(6) - Mn(1)	148.96(12)	C(15)-O(4)-Mn(2)	95.04(9)
O(5)-Mn(2)-N(1)	88.34(5)	C(15)-O(4)-Mn(1)	128.26(10)
O(1) - Mn(2) - N(1)	105.10(5)	Mn(2)-O(4)-Mn(1)	105.74(4)
O(4) - Mn(2) - N(1)	151.12(5)	O(3)-C(15)-O(4)	120.69(15)
O(5)-Mn(2)-N(2)	159.42(5)	O(6)-C(19)-O(5)	125.12(15)
O(1)-Mn(2)-N(2)	88.58(5)		

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

Table 4

Selected bond lengths (Å) and angles (°) for complex 3

Mn(1)-O(1)	2.1387(8)	O(2)-C(7)	1.2506(12)
Mn(1)-O(2)#1	2.1183(8)	N(1)-C(1)	1.3273(14)
Mn(1)-N(1)	2.3499(9)	N(1)-C(6)	1.3554(13)
O(1)-C(7)	1.2519(13)		
O(2)#4-Mn(1)-O(2)#1	99.63(4)	C(7)-O(1)-Mn(1)	145.24(7)
O(2)#1-Mn(1)-O(1)	98.24(3)	C(7)-O(2)-Mn(1)#1	144.24(7)
O(2)#4-Mn(1)-O(1)	85.32(3)	C(1)-N(1)-Mn(1)	125.84(7)
O(1)#2-Mn(1)-O(1)	174.51(4)	C(6)-N(1)-Mn(1)	116.60(6)
N(1)#2-Mn(1)-N(1)	70.88(4)	O(2)-C(7)-O(1)	126.41(9)
O(2)#4-Mn(1)-N(1)	94.83(3)	O(1)#2-Mn(1)-N(1)	89.93(3)
O(2)#1-Mn(1)-N(1)	165.28(3)	O(1)-Mn(1)-N(1)	85.59(3)

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

3 days at about 423.15 K, and then the mixture was cooled to room temperature naturally. Yellow single crystals were obtained (yield = about 78% based on Mn). *Anal.* Calc. for $\{Mn_{3}^{II}(tp)_{6/2}^{-1}(bpy)_{2} \cdot (dmf)\}_{n}$ (2): C, 54.14; H, 3.38; N, 6.72. Found: C, 54.28; H, 3.51; N, 6.83%. IR (KBr, cm⁻¹): 1576.76 s, 1474.78 m, 1439.04 s, 1380.86 s, 1313.63 m, 1151.88 m, 1095.69 w, 1058.42 w, 1018.52 m, 971.55 w, 803.94 m, 760.23 s, 668.17 w, 649.94 m, 628.01 w, 524.9 m.

2.2.3. $\{Mn^{II}(tp)(phen)\}_n$ (**3**)

A solution of MnCl₂ (0.136 g, 1 mmol) in 10 ml of water was added to a solution of terephthalic acid (0.249 g, 1.5 mmol) and 1,10-phenanthroline (0.198 g, 1 mmol) in DMF (10 ml), stirring for about 2 h at room temperature. Then the resulting solution was transferred into a Teflon-Steel autoclave inside a programmable electric furnace reactor. The mixed-solvo-thermal reaction lasted for about 3 days at about 423.15 K, and then the mixture was cooled to room temperature naturally. Yellow single crystals were obtained (yield = about 82% based on Mn). *Anal.* Calc. for {Mn^{II}(tp)(phen)}_n (**3**): C, 60.17; H, 3.01; N, 7.01. Found: C, 60.31; H, 3.19; N, 7.12%. IR (KBr, cm⁻¹): 1598.26 s, 1514.15 m, 1495.77 w, 1425.86 m, 1387.00 s, 1100.70 w, 1046.49 w, 1024.00 w, 890.79 w, 863.80 w, 846.12 m, 807.17 m, 770.50 w, 750.31 s, 729.00 m, 633.97 w, 505.50 m.

2.3. Crystallographic data collection and refinement

X-ray diffraction measurements were performed on a Bruker SMART diffractometer equipped with a CCD area detector with graphite-monochromated Mo K α radiation (K α = 0.71073 Å) at about 290(2) K. The reflections were successfully indexed by an automated indexing routine built in the SMART program [10]. The solutions were solved by direct methods and refined by full-matrix least-squares calculations on F^2 with SHELX-97 [11]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the calculated positions using the riding model. Crystallographic data and refinement details for the structural analyses of all the complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations for complexes 1–3 in are in Tables 2–4, respectively.



Fig. 1. (a) Perspective view of the asymmetry unit of 1; (b) perspective view of the zigzag one-dimensional chain of 1; (c) crystal packing diagram of 1 along the *c* axis, showing the hydrogen-bond interactions between the one-dimensional chains.

3. Results and discussion

3.1. Description of the crystal structures of complexes 1-3

3.1.1. $\{Mn^{II}(tp)(bpy)(H_2O)\}_n$ (1)

X-ray single crystal structure determination reveals that complex **1** is a neutral one-dimensional infinite zigzag coordination chain. Each Mn^{II} center coordinates to two N donors of one 2,2'bipyridine, three oxygen atoms belonging to two different carboxyl groups of two different terephthalic acid molecules and one water molecule, forming a distorted octahedral geometry as shown in Fig. 1a. Then, two neighboring Mn^{II} centers are connected by a terephthalic dianion which acts as a long bridge through the benzene ring as shown in Scheme 1. The 2,2'-bipyridine molecule acts as a terminal ligand which prevents the chain from growing in a straight forward direction, and making it into a zigzag chain. (Fig. 1b). Selected bond lengths and angles are listed in Table 2.



Fig. 2. (a) Perspective view of the trinuclear node of 2; (b) perspective view of the two-dimensional sheet of **2**, viewing along the *b* axis; (c) crystal packing diagram of **2** along the *c* axis, showing the $\pi \cdots \pi$ stacking interaction between two sheets.

Analysis of the crystal packing of **1** in the unit cell indicates that there is one type of independent inner-chain O–H···O hydrogen bond and one kind of independent inter-chain O–H···O hydrogen bond (Table 3). The former is formed by the O–H group of the coordinated water molecule with the uncoordinated oxygen atom of the neighboring carboxyl groups of the terephthalic dianion in an asymmetric unit with a D···A distance of 2.6749(18) Å and an O– H–O angle of 147.1°. The inter-chain O–H···O hydrogen bonds are formed by the O–H group of the coordinated water molecule in one coordination chain with one of the coordinated oxygen atoms of the carboxyl groups of the terephthalic dianion in the adjacent coordination chain, with a D···A distance of 2.7111(17) Å and an O–H–O angle of 165(3)°.

3.1.2. $\{Mn_{3}^{II}(tp)_{6/2}(bpy)_{2} \cdot (dmf)\}_{n}$ (2)

The crystal structure analysis shows that complex **2** adopts a 2D framework. The 2D skeleton is formed by Mn ions as nodes and tp

dianions as spacers, through coordination bonds. At each node there are three Mn^{II} atoms that are in a linear arrangement with $Mn \cdots Mn$ distances of 3.266 Å (Fig. 2a), all of which have a distorted octahedral geometry and two adjacent octahedrons share a triangular face. The middle Mn^{II} atom is coordinated by six oxygen atoms (Mn-O = 2.038(3)-2.254(3) Å) belonging to six different tp carboxylate groups, while each of the two terminal Mn^{II} atoms is coordinated by four oxygen atoms (Mn-O = 2.038(3)-2.254(3) Å) belonging to four different tp carboxylate groups and two nitrogen atoms (Mn-N = 2.038(3)-2.254(3) Å) of one chelating 2,2'-bipyridine ligand.

Each three Mn^{II} -atoms-cluster node is bridged by six tp ligands in six directions in the 010 plane with two 2,2'-bipyridine ligands upon and down the plane, respectively, and the angles between the two directions are nearly 60° (Fig. 2b). Every three nodes are connected by three tp ligands along the 100, 101 and 201 planes to form an equilateral triangle. Then the remarkable two-dimensional



Fig. 3. (a) Perspective view of the asymmetry unit of **3**; (b) perspective view of the one-dimensional {Mn}_n chain of **3**; (c) perspective view of the three-dimensional framework of **3** along the *c* axis.

sheets are formed by the equilateral triangle arrays (Fig. 2b). The distance between two adjacent 2,2'-bipyridine ligands of two neighboring sheets is 3.446 Å, which is within the range of $\pi \cdots \pi$ stacking interactions, 3.3–3.7 Å. The $\pi \cdots \pi$ stacking interactions between the two sheets connects the sheets into a 3D coordination polymer (Fig. 2c), the interspace of which is filled by isolated DMF molecules.

3.1.3. $\{Mn^{II}(tp)(phen)\}_n$ (**3**)

The crystal structure analysis shows that there is one terephthalic ligand, one 1,10-phenanthroline ligand and one Mn^{II} atom in each asymmetric unit of complex **3**, which build up a threedimensional structural framework. Each Mn^{II} atom has a distorted octahedral geometry, being coordinated to four oxygen atoms (Mn-O = 2.106(2)-2.145(2) Å) belonging to four different carboxyl groups of four different terephthalic dianions, and two nitrogen atoms of one phen molecule (Mn-N = 2.323(2)-2.368(2) Å)(Fig. 3a).

The bidentate carboxylate groups, in pairs, belong to two different terephthalic dianions and, acting as short bridges, bridge two neighboring Mn atoms to form an eight-membered ring in a chair configuration. One of the two Mn atoms and another neighboring Mn atom are bridged by two other bidentate carboxylate groups in a pair to form another eight-membered ring plane. The two planes cross with angles of nearly 60°, and each two crossed eight-membered rings alternatively bridge the neighboring Mn atoms to form 1D $[Mn_2(CO_2)_2(phen)_2]_n$ chains with Mn···Mn distances of 4.7894 Å (Fig. 3b). Then the terephthalic dianions, acting as long bridges via the benzene ring in the directions of the two basal eight-membered ring planes, link $[Mn_2(CO_2)_2(phen)_2]_n$ chains to form the 3D structure of **3** and 1D channels along the 1D $[Mn_2(CO_2)_2(phen)_2]_n$ chains.

The 1D channels along the 1D $[Mn_2(CO_2)_2(phen)_2]_n$ chains in **3** are filled with coordinated 1,10-phenanthroline molecules. It should be pointed out that the mean distance of two neighboring face-to-face stacked 1,10-phenanthroline molecules is about 3.629 Å, which is within the range of $\pi \cdots \pi$ stacking interactions, 3.3–3.7 Å.

3.2. Magnetic properties

The variation of the molar magnetic susceptibilities χ_M was investigated for compounds **1–3** in the temperature range 2–300 K at a field of 1000 Oe. The study of the temperature dependent magnetic susceptibilities revealed that all the compounds show antiferromagnetic behaviour.

The thermal variation of χ_{M}^{-1} and $\chi_{M}T$ of **1** are displayed in Fig. 4a. According to the $\chi_{M}^{-1}-T$ curve, the magnetic behavior of **1** follows the Curie–Weiss law $\chi_{M} = C/(T - \theta)$ with a Curie constant C value of 4.14 cm³ K mol⁻¹ and a Weiss temperature θ of -0.70 K. The value of $\chi_{M}T$ at 300 K is 4.64 cm³ K mol⁻¹ per Mn^{II}, which is slightly above the expected value for the *S* = 5/2 spin-only ground state per couple of uncorrelated Mn^{II} centers (4.35 cm³ K mol⁻¹). This value decreases smoothly to close to 3.35 cm³ K mol⁻¹ at 2 K. Such magnetic behavior is typical for an antiferromagnetic coupling between the Mn^{II} ions in the chain. The magnetic susceptibility of **1** has been fitted to the Fisher model [12] of the isotropic Heisenberg antiferromagnet, and later modified by Wagner and Friedberg [13] for a Mn²⁺ system of spin 5/2, which is

$$\chi = \frac{NS(S+1)}{3kT}g^2\beta^2 \frac{1-u(K)}{1+u(K)}$$
(1)

where u(K) is $1/K - \operatorname{coth}(K)$, K = 2JS(S + 1)/kT, g = 2, S = 5/2 for Mn(II) and *N*, β , *K*, *g* and *T* have their usual meanings. Due to the interac-

tion between adjacent chains, the fit function can be modified to include the inter-chain coupling [14]. The function, therefore, is

$$\chi_{\rm M} = \frac{\chi}{1 - (2zJ'/Ng^2\beta^2)\chi} \tag{2}$$

where *J'* is the inter-chain exchange coupling constant and *z* is the number of the nearest neighbor chains. The best fitting for the data in the range of 2–300 K gives $J = -0.035 \text{ cm}^{-1}$, $zJ' = +0.028 \text{ cm}^{-1}$ and g = 2.00, with $R = 4.2 \times 10^{-6}$, $\left[R = \left[\sum (\chi_{obs} - \chi_{calc})^2 / \sum (\chi_{obs})^2\right]\right]$.

According to the $\chi_{\rm M}^{-1}-T$ curve, the magnetic susceptibility data for **2** also fit well to the Curie–Weiss law in the range 2–300 K and give a Curie constant *C* value of 10.8 cm³ K mol⁻¹ and a Weiss temperature θ of –1.81 K. The value of $\chi_{\rm M}T$ at 300 K is 10.85 cm³ K mol⁻¹ per tri-Mn^{II} unit. These value decreases smoothly to close to 7.83 cm³ K mol⁻¹ at 2 K. Such magnetic behavior shows antiferromagnetic couplings between the Mn^{II} ions.



Fig. 4. (a) The thermal variation of χ_{M}^{-1} and $\chi_{M}T$ of **1**; (b) the thermal variation of χ_{M}^{-1} and $\chi_{M}T$ of **2**; (c) the thermal variation of χ_{M}^{-1} and $\chi_{M}T$ of **3**.

The magnetic susceptibility data for **3** also follows the Curie–Weiss law in the range 12–300 K ($C = 5.10 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -34.4 \text{ K}$). At 300 K, the $\chi_M T$ value of **3** is 4.53 cm³ K mol⁻¹, which is slightly above the expected value for S = 5/2 of a spin-only ground state per couple of uncorrelated Mn^{II} centers (4.35 cm³ K mol⁻¹). This value decreases smoothly to close to 0.18 cm³ K mol⁻¹). This value decrease of $\chi_M T$ is attributed to antiferromagnetic interactions between the Mn^{II} ions. As mentioned above, the 3D structure of **3** can be viewed as [Mn₂(CO₂)₂(phen)₂]_n chains linked by a long bridge, the terephthalic dianions. So we can evaluate the value of the couplings via the Fisher model as in the case of **1**, where zJ' is the inter-chain interactions of the neighboring [Mn₂(CO₂)₂(phen)₂]_n chains. The best fitting for the data in the range 15–300 K gives $J = -0.53 \text{ cm}^{-1}$, $zJ' = -0.69 \text{ cm}^{-1}$ and g = 2.09, with $R = 3.2 \times 10^{-5}$, $\left[R = \left[\sum (\chi_{obs} - \chi_{calc})^2 / \sum (\chi_{obs})^2\right]\right]$.

Comparing the magnetic properties of **1–3**, especially the Weiss constants (-0.70, -1.81 and -34.4 K, respectively), it is obvious that the antiferromagnetic coupling in **1** and**2** is much weaker than that in **3**, which mainly results from the difference between their structures. Compound **1** can be viewed as having isolated Mn^{II} nucleii and **2** can be viewed as isolated trinuclear Mn^{II} clusters separated by the terephthalate ligands, which act as long bridges via the benzene ring, while compound **3** can be regarded as infinite 1D Mn^{II} chains linked by short three-atom O–C–O bridges.

4. Conclusion

Three Mn^{II}-terephthalate coordination polymers have been synthesized with different terminal ligands, and the crystal structure analyses show that the compounds are in the form of 1D infinite chains or 2D sheets with 2,2'-bipyridine as a terminal ligand, while the compound with 1,10-phenanthroline as a terminal ligand has a 3D framework. Despite the different structures, a magnetic investigation indicates that all three coordination polymers show antiferromagnetism. Further works are focused on investigation of the influence of other multidentate ligands and terminal ligands to the structures and properties of the coordination polymers.

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Appendix A. Supplementary data

CCDC 641261, 642728 and 644541 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2008.04.029.

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