A series of manganese-carboxylate coordination polymers exhibiting diverse magnetic properties[†]

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Received 22nd May 2008, Accepted 11th July 2008

First published as an Advance Article on the web 21st August 2008 DOI: 10.1039/b808691e

The hydrothermal reactions of an asymmetrical 4-(4-carboxyphenylamino)-3,5-dinitrobenzoic acid (H₂cpdba), MnCl₂·4H₂O, or together with 2,2'-bipyridine (2,2'-bpy) or 4,4'-bipyridine (4,4'-bpy) afford three novel molecule-based magnetic coordination polymers [Mn(cpdba)]_n (1), {[Mn₂(cpdba)₂(2,2'-bpy)₂(H₂O)₂]·H₂O}_n (2) and {[Mn₂(cpdba)₂(4,4'-bpy)]·2H₂O}_n (3). Compound 1 has a 3D acentric coordination network containing carboxylate-bridged 1D ladder-like manganese chains with spin-canted antiferromagnetism (J = -3.51 cm⁻¹ for the coupling along the ladder legs, and zJ' = 0.22 cm⁻¹ for coupling along the ladder rungs), whereas compounds 2 and 3 crystallize in the centrosymmetric space groups $P\overline{1}$ and C2/c, respectively. 2 exhibits a 1D chain structure, which is extended into a 3D supramolecular network by π - π stacking interactions, while 3 features a quite complex 3D network built up from the cpdba²⁻ and 4,4'-bpy spacers as well as the carboxylate-bridged Mn(II) chains. Both 2 and 3 show weak antiferromagnetic coupling interactions (J = -0.55 cm⁻¹ for 2), and a field-induced spin-flop magnetic transition can also be observed in 2 at *ca.* 3.2 T at 2 K.

Introduction

During past decades, a considerable research effort has been focused on the design and synthesis of molecule-based magnetic materials due to their impressive structural diversity and intriguing physical properties as well as complicated magneto-structural correlations.¹⁻⁴ Judicious choice of appropriate molecular building blocks can effectively mediate the magnetic interaction between the paramagnetic metal ions, and provide a powerful means to create a rich variety of new materials with interesting magnetic properties, such as spin-canting, metamagnetic transition, spin-flop transition, *etc.*^{5,6} Despite the great progress in the construction of magnetic molecular materials, it still remains a challenge to obtain extended networks with spontaneous magnetizations and predictable magnetic properties.

One origin for a spontaneous magnetization may arise from spin-canting, which is usually due to the antisymmetric exchange and/or the single-ion anisotropy.^{7a} Since the low symmetry of the crystal structures is beneficial to the occurrence of the antisymmetric exchange,⁸ and may afford a significantly increased anisotropy barrier,⁹ it is possible to induce spin-canting by lowering the symmetry of the systems. Within the realm of crystal engineering, the unsymmetrical organic ligands have been utilized as pre-chiral or non-centrosymmetric building blocks to construct acentric materials.¹⁰ If the asymmetry of the organic ligands can

be transferred to magnetic entities when they link paramagnetic metal ions, especially the metal ions with a large anisotropy, to form ordered structures, the probability of spin-canting should increase. Aiming at optimizing the conditions for the occurrence of spin-canting based on the asymmetrical transference and consequently finding an effective way to the construction of molecular materials with spontaneous magnetizations, we synthesized a Vtype asymmetrical 4-(4-carboxyphenylamino)-3,5-dinitrobenzoic acid (H₂cpdba) ligand, in which the presence of two carboxylic groups not only can supply diverse super-exchange pathways being attributed to favourable orbital interactions between the oxygen p and metal d orbitals, but can also be easily combined with other ancillary ligands.^{11,12} Herein, we present the syntheses, crystal structures and magnetic behaviour of three novel metal-organic hybrid networks having the molecular formula $[Mn(cpdba)]_n$ (1), $\{[Mn_2(cpdba)_2(2,2'-bpy)_2(H_2O)_2] \cdot H_2O\}_n$ (2) and { $[Mn_2(cpdba)_2(4,4'-bpy)] \cdot 2H_2O]_n$ (3). 2,2'-bipyridine (2,2'bpy) or 4,4'-bipyridine (4,4'-bpy) are introduced in order to explore the effect of co-ligands on the structural symmetry. It is interesting to note that a 3D acentric coordination network containing carboxylate-bridged 1D ladder-like manganese chains (1), which shows spin-canted antiferromagnetism, can be obtained in the absence of co-ligands. In the presence of coligands, compounds 2 and 3, with the centrosymmetric space groups $P\overline{1}$ and C2/c can be obtained, respectively. The former exhibits a 1D chain structure, which is extended into a 3D supramolecular network by π - π stacking interactions arising from 2,2'-bpy ancillary ligands, while the latter features a quite complex 3D network built up from cpdba2- and 4,4'-bpy spacers as well as the carboxylate-bridged Mn(II) chains. Both 2 and 3 show weak antiferromagnetic coupling interactions, and a fieldinduced spin-flop transition can also be observed in 2 at ca. 3.2 T at 2 K.

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[†] Electronic supplementary information (ESI) available: IR spectra for 1–3 and temperature-dependent ac susceptibility data for 1. CCDC reference numbers 679474–679476. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808691e

Table 1 Crystal data and structure refinement for compounds 1–3

	1	2	3
Formula	$C_{14}H_7MnN_3O_8$	$C_{48}H_{36}Mn_2N_{10}O_{19}$	$C_{38}H_{26}Mn_2N_8O_1$
M_r	400.17	1166.75	992.55
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	Iba2	$P\overline{1}$	C2/c
a/Å	18.3259(15)	9.4695(14)	26.7150(19)
b/Å	25.300(2)	15.348(2)	12.9166(7)
c/Å	7.5240(7)	17.220(2)	25.9898(19)
$\alpha / ^{\circ}$	90.00	93.952(5)	90.00
$\beta/^{\circ}$	90.00	100.876(7)	114.048(3)
γ°	90.00	102.557(5)	90.00
$V/Å^3$	3488.5(5)	2383.2(6)	8189.8(9)
Ζ	8	2	8
$D_{\rm calcd}/{ m g~cm^{-3}}$	1.524	1.618	1.603
μ/mm^{-1}	0.804	0.623	0.706
F(000)	1608	1180	4000
GOF	0.994	0.999	1.003
Collected reflections	13311	18674	31179
Unique reflections (R_{int})	3860 (0.0535)	10 746 (0.0449)	9378 (0.0339)
Observed reflections $[I > 2\sigma(I)]$	3194	6376	8195
Refined parameters	239	719	597
$R_1^a/WR_2^{b}[I>2\sigma(I)]$	0.0541/0.1890	0.0747/0.1870	0.0623/0.1900
R_1^a/WR_2^b (all data)	0.0678/0.2013	0.1296/0.2324	0.0699/0.1986

Experimental

Materials and methods

All chemicals and solvents were of reagent grade and were used as received. IR spectra were recorded with a Spectrum One FT-IR spectrophotometer as KBr pellets in the range 4000–400 cm⁻¹. Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. Magnetic susceptibility data were measured using a Quantum Design PPMS-9T system. Diamagnetic corrections were made for the sample holder and sample. 4-(4-Carboxyphenylamino)-3,5-dinitrobenzoic acid (H₂cpdba) was synthesized according to the literature.¹³

[Mn(cpdba)]_{*n*} **(1).** MnCl₂·4H₂O (0.25 mmol, 0.049 g), H₂cpdba (0.125 mmol, 0.044 g), and NaOH (0.25 mmol, 0.010 g) were mixed in 8 mL of distilled water, and the solution was stirred for 1 h and transferred into a 23 mL Teflon-lined autoclave at 160 °C for 5 d and then slowly cooled to room temperature. Dark-red needle crystals of **1** were obtained in 20% yield based on manganese. Anal. calcd for C₁₄H₇N₃O₈Mn ($M_r = 400.17$): C 42.02, H 1.76, N 10.50. Found: C 42.46, H 2.87, N 10.47. The slightly high hydrogen content might result from the water absorption of **1** within its porous structure. FT-IR (KBr, cm⁻¹): 3434 m, 3357 m, 1625 m, 1601 s, 1537 m, 1499 m, 1447, 1390 s, 1384 vs, 1357 m, 1290 m, 1183 m, 1113 w, 1099 w, 1015 w, 866 w, 783 m, 752 w, 722 w, 705 w, 677 w, 618 w, 593 w, 484 w, 444 m, 417 w.

{[Mn₂(cpdba)₂(2,2'-bpy)₂(H₂O)₂]·H₂O}_{*n*} (2). The procedure was the same as that for 1 except 2,2'-bpy (0.125 mmol, 0.020 g) was added. Orange sheet crystals of 2 were obtained in 34% yield based on manganese. Anal. calcd for C₄₈H₃₆N₁₀O₁₉Mn₂ ($M_r = 1166.75$): C 49.41, H 3.11, N 12.01. Found: C 49.29, H 3.23, N 11.92. FT-IR (KBr, cm⁻¹): 3429 br, 3333 m, 1622 s, 1602 s, 1532 s, 1474 w, 1441 m, 1393 vs, 1373 s, 1349 m, 1285 m, 1180 w, 1101 w,

1017 w, 932 w, 874 w, 851 w, 775 m, 768 m, 737 w, 724 w, 704 w, 673 w, 653 w, 627 w, 548 w, 503 w, 454 w, 414 w.

 $\{[Mn_2(cpdba)_2(4,4'-bpy)]\cdot 2H_2O\}_n$ (3). The procedure was the same as that for 1 except 4,4'-bpy (0.125 mmol, 0.020 g) was added. Dark-red block crystals of 3 were obtained in 24% yield based on manganese. Anal. calcd for $C_{38}H_{26}N_8O_{18}Mn_2$ ($M_r = 992.55$): C 45.99, H 2.64, N 11.29. Found: C 46.37, H 2.98, N 11.47. FT-IR (KBr, cm⁻¹): 3406 br, 3314 w, 3077 w, 1660 s, 1610 m, 1599 vs, 1562 s, 1509 m, 1484 w, 1438 w, 1408 m, 1377 s, 1344 m, 1277 m, 1218 w, 1182 w, 1101 w, 1064 w, 1040 w, 1013 w, 931 w, 869 w, 834 w, 809 m, 773 m, 757 w, 728 w, 700 w, 683 w, 622 w, 576 w, 510 w.

Single-crystal structure determination

The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. CrystalClear software¹⁴ was used for data reduction. The structures were solved by direct methods and refined by full-matrix least-squares procedure on F^2 using the SHELXS-97 and SHELXL-97 programs.¹⁵ All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms attached to carbon atoms were geometrically placed and refined using a riding model. However, the H atoms of the water molecules in **1–3** have not been included in the final refinement. The crystallographic data are summarized in Table 1 and selected bond distances and angles of the three compounds are listed in Table 2, Table 3 and Table 4, respectively.

Results and discussions

Structure of 1

The single-crystal X-ray diffraction study reveals that compound 1 has a 3D acentric coordination network. The asymmetric unit

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

Mn1–O5A	2.055(4)	Mn1–O8D	2.166(4)
Mn1–O6	2.094(4)	Mn1–O7B	2.207(4)
Mn1–O7C	2.141(4)	Mn1–O8B	2.693(3)
O5A-Mn1-O6	104.9(2)	O6-Mn1-O7C	86.95(17)
O5A-Mn1-O7C	112.72(17)	O6-Mn1-O7B	82.73(17)
O5A-Mn1-O7B	95.40(17)	O7C-Mn1-O7B	151.71(13)
O5A-Mn1-O8D	94.05(18)	O7C-Mn1-O8D	83.74(15)
O6–Mn1–O8D	160.94(19)	O8D-Mn1-O7B	97.81(15)

Symmetry codes: (A) x, 1 - y, 0.5 + z; (B) 1.5 - x, 0.5 - y, 0.5 + z; (C) 1.5 - x, 0.5 + y, z; (D) 0.5 + x, 0.5 + y, 0.5 + z.

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

Mn1–N7	2.256(4)	Mn1–N8	2.255(4)
Mn1–O2	2.137(3)	Mn1–O10	2.107(4)
Mn1–O15A	2.113(4)	Mn1–O1w	2.410(7)
Mn2–N9	2.245(4)	Mn2-N10	2.233(4)
Mn2–O7B	2.230(3)	Mn2–O8B	2.288(4)
Mn2–O9	2.112(4)	Mn2–O2w	2.145(4)
N7–Mn1–O1w	93.8(2)	N8-Mn1-N7	72.69(17)
N8–Mn1–O1w	76.0(2)	N9-Mn2-O8B	93.84(15)
N10-Mn2-N9	73.00(15)	N10-Mn2-O8B	97.66(14)
O2-Mn1-N7	97.76(15)	O2-Mn1-N8	110.23(16)
O2-Mn1-O1w	168.1(2)	O7B-Mn2-N9	88.13(14)
O7B-Mn2-N10	148.76(14)	O7B-Mn2-O8B	58.17(13)
O9-Mn2-N9	93.40(15)	O9-Mn2-N10	92.22(15)
O9-Mn2-O7B	114.02(14)	O9-Mn2-O8B	169.12(14)
O9-Mn2-O2w	91.76(14)	O10-Mn1-N7	162.48(15)
O10-Mn1-N8	92.57(15)	O10-Mn1-O2	96.21(14)
O10-Mn1-O15A	101.19(16)	O10-Mn1-O1w	73.0(2)
O15A-Mn1-N7	88.81(17)	O15A-Mn1-N8	152.32(16)
O15A-Mn1-O2	92.18(16)	O15A-Mn1-O1w	85.1(2)

Symmetry codes: (A) -x, -y, 1 - z; (B) x, y, -1 + z.

Table 4Selected bond lengths (Å) and angles (°) for 3

Mn1–O1	2.146(2)	Mn2-O15	2.591(2)
Mn1–O10B	2.110(3)	Mn2-O16	2.210(2)
Mn1–O16	2.350(2)	Mn3–N7	2.253(3)
Mn2–O2	2.147(2)	Mn3-O15	2.328(2)
O1-Mn1-O16	78.16(9)	O10B-Mn1-O16	82.74(10
O2-Mn2-O15	84.04(10)	O2-Mn2-O16	87.43(10
O15-Mn2-O16	53.42(9)	N7-Mn3-O15	93.60(10

Symmetry codes: (B) 0.5 + x, -0.5 + y, z.

of 1 contains a cpdba²⁻ ligand and a Mn²⁺ ion as illustrated in Fig. 1. The Mn²⁺ ion is located in a distorted octahedral environment surrounded by a chelating carboxylate group and four monodentate carboxylate groups from different cpdba2ligands, respectively. Five Mn-O bond lengths are in the range of 2.055(4)–2.207(4) Å and the sixth one is 2.693(3) Å. Although it is rather longer than the other five bonds, similar Mn-O bond lengths have been reported previously.¹⁶ The cpdba²⁻ ligand in 1 shows a μ_5 -coordination mode. The carboxylate group near the nitryl groups adopts a bidentate bridging mode to link two Mn²⁺ ions, while another carboxylate group binds to three Mn²⁺ ions in a μ_3 - η^2 bridging mode (Scheme 1a). Such a μ_5 -binding mode is still very scarce despite the fact that numerous polycarboxylate complexes have been reported.¹⁷ Each Mn²⁺ ion is bridged by the carboxylate groups of the cpdba²⁻ ligands to form a 1D $[Mn(CO_2)_2]_n$ ladder-like chain along the c axis with $Mn \cdots Mn$ distances of *ca*. 3.74 Å (along the *a* axis) and 3.86 Å (along the *c*



Fig. 1 ORTEP drawing of the molecular structure of **1** (50% probability level). Solvent water molecules and all hydrogen atoms have been omitted for clarity. Symmetry code: (A) x, 1 - y, 0.5 + z; (B) 1.5 - x, 0.5 - y, 0.5 + z; (C) 1.5 - x, 0.5 + y, z; (D) 0.5 + x, 0.5 + y, 0.5 + z.



Scheme 1 Coordination modes of the cpdba²⁻ ligand in 1 (a), 2 (b and c), 3 (a and d).

axis) as shown in Fig. 2, (left). These 1D ladder-like chains acting as secondary building units (SBUs), are further interconnected through (2,6-dinitrophenyl)-phenyl-amino moieties of the cpdba²⁻ molecules to generate an extended 3D open framework in which there are 1D elliptic channels of 5.719 × 8.983 Å² (measured between opposite hydrogen atoms) without the solvents residing along *c* axis, as shown in Fig. 2, (right). It is worth mentioning that no 3D polycarboxylate–Mn coordination polymers containing 1D [Mn(CO₂)₂]_n ladders have been reported so far, although there are a lot of coordination polymers in which 1D chains act as SBUs.^{17a,18}



Fig. 2 1D Mn(CO₂)₂ ladder chain (left) and the 3D open framework with 1D channels extending along the c axis (right) in **1**.

Structure of 2. As shown in Fig. 3, the asymmetric unit of 2 contains two Mn2+ ions, two 2,2'-bpy ligands, two cpdba2- ligands, two coordinated water molecules and one lattice water molecule. Mn1 has a distorted octahedral coordination environment with a chelating 2,2'-bpy ligand, three carboxylate groups from different cpdba²⁻ ligands in a monodentate coordination mode, and one water molecule. Similarly, Mn2 also has a distorted octahedral geometry with two nitrogen atoms from a 2,2'-bpy, a chelating and a monodentate carboxylate group from two different cpdba2ligands, and one water molecule. The cpdba2- ligand exhibits two kinds of bridging modes in the structure of 2. One cpdba²⁻ ligand connects three manganese ions with two carboxylate groups in monodentate and bridging modes, respectively (Scheme 1b), while another binds to two Mn²⁺ ions by two carboxylate groups in monodentate and chelating coordination modes (Scheme 1c). The Mn1 and Mn2 ions are linked through one carboxylate group in syn-anti mode, giving rise to a dinuclear subunit. These dinuclear units are connected by a (2,6-dinitrophenyl)phenyl-amino spacer to form a 1D polymeric chain (Fig. 4, top). Interestingly, there are inter-chain π - π stacking interactions, which arise from 2,2'-bpy ligands. The 2,2'-bpy ligand coordinated to the Mn1 atoms employs its single-pyridyl ring to form π - π stacking



Fig. 3 ORTEP drawing of the molecular structure of **2** (30% probability level). All hydrogen atoms and lattice water molecules have been omitted for clarity. Symmetry codes: (A) -x, -y, 1 - z; (B) x, y, -1 + z.



Fig. 4 1D polymeric chain (top) and 3D network constructed by π - π stacking interactions between 1D chains (bottom) in **2**. All hydrogen atoms and solvent water molecules have been omitted for clarity. The dashed lines represent π - π stacking interactions.

with a centroid-to-centroid distance of 3.782 Å and an inter-planar pyridine distance of 3.56 Å, whereas another 2,2'-bpy ligand coordinated to Mn2 atoms employs its double-pyridyl ring to form a π - π interaction with a centroid-to-centroid distance of 3.645 Å and an inter-planar distance of 3.51 Å. Finally, these 1D chains interweave with each other to form a 3D supramolecular network as shown in Fig. 4, bottom.

Structure of 3. The asymmetric unit of compound 3 contains three crystallographically independent Mn²⁺ ions, two cpdba²⁻ ligands, one 4,4'-bpy ligand and two lattice water molecules (Fig. 5). All Mn²⁺ ions have distorted octahedral coordination environments. Mn1 is surrounded by six carboxylate oxygen atoms from six cpdba2- ligands, Mn2 is coordinated by one carboxylate group in a chelating mode, three carboxylate groups in a monodentate mode and one pyridyl nitrogen atom, while Mn3 is coordinated by four carboxylate oxygen atoms from four cpdba2- ligands, and two nitrogen atoms from two 4,4'-bpy ligands (Fig. 6, top). Each Mn1 atom is bridged to both Mn2 by two *syn–syn* carboxylate bridges and one μ_2 -O bridge from the μ_3 carboxylate group to give a trinuclear unit. This trinuclear unit is further connected to two Mn3 atoms through one syn-anti carboxylate bridge and one μ_2 -O bridge from the μ_3 -carboxylate group, finally resulting in the formation of $1D [Mn(CO_2)_2]_n$ chains with Mn2-Mn1-Mn2-Mn3 repeat units (Fig. 6, top), in which the Mn1 \cdots Mn2 and Mn2 \cdots Mn3 distances are 3.58 and 4.15 Å, the Mn1-O16-Mn2 and Mn2-O15-Mn3 bond angles are 103.36 and 114.88°, respectively. The 4,4'-bpy ligand coordinates to Mn2 and Mn3 through two terminal N atoms, which may hold the 1D $[Mn(CO_2)_2]_n$ chains together in a 2D layer as illustrated in Fig. 6, bottom. The whole structure of 3 can be described as quite a complex 3D network constructed by cpdba²⁻ and 4,4'-bpy ligand (ESI, Fig. S4).[†] It is interesting to note that the cpdba²⁻ ligand also adopts two types of bridging modes in 3, one cpdba²⁻ anion coordinates to four Mn²⁺ ions in the bidentate bridging mode (Scheme 1d), while another adopts the rare μ_5 -bridging mode like that observed in 1.



Fig. 5 ORTEP drawing of the molecular structure of compound **3** (30% probability level). All solvent water molecules and hydrogen atoms have been omitted for clarity.

Magnetic properties

The thermal variations of the χ_m and $\chi_m T$ products obtained at an applied field of 1 T for 1 are shown in Fig. 7, top. At room temperature, the $\chi_m T$ value is 3.80 emu K mol⁻¹, which is lower than that expected for an isolated Mn²⁺ ion (4.375 emu K mol⁻¹ for S = 5/2 with g = 2.0), suggesting the presence of an appropriate antiferromagnetic interaction.¹⁹ As the temperature



Fig. 6 1D $[Mn(CO_2)_2]_n$ chain with Mn2–Mn1–Mn2–Mn3 repeat units (top). The 4,4'-bpy ligands connect the 1D $[Mn(CO_2)_2]_n$ chains to form a 2D layer in **3** (bottom). Symmetry codes: (A) –*x*, *y*, 0.5 – *z*; (B) 0.5 + *x*, -0.5 + *y*, *z*.



Fig. 7 Temperature dependence of the χ_m and $\chi_m T$ products of compound 1 within the whole temperature range (top), as well as at low temperature and different applied fields (bottom).

is lowered from 300 K to 75 K, there is a smooth decrease in $\chi_m T$, whereas below 75 K, the $\chi_m T$ value decreases sharply and reaches 0.12 emu K mol⁻¹ at 2 K. The Weiss constant θ , obtained by fitting the reciprocal magnetic susceptibility $(1/\chi_m)$ to the Curie–Weiss law above 40 K, is –38.6 K. The structural analysis indicates that the minimum distance between adjacent 1D [Mn(CO₂)₂]_n ladder chains is *ca.* 13.55 Å (Mn ··· Mn). Such a long distance across the cpdba²⁻ ligand plays a negligible role in propagating magnetic exchanges, therefore the magnetic exchanges within the $[Mn(CO_2)_2]_n$ ladder are dominant. If we neglect the comparatively weak magnetic coupling interaction mediated by the anti-anti carboxylate groups²⁰ along the diagonal, there are two predominant super-exchange pathways within the chain: one connects Mn²⁺ ions *via* two carboxylate groups in μ_3 - η^2 bridging mode (the rungs of the ladder) with the Mn-O-Mn bond angle of 100.08°, which lies in the range that ferromagnetic couplings can be expected,²¹ and another one links Mn²⁺ ions through one *svn–svn* and one μ_3 - η^2 bridging carboxylate groups into uniform linear chains (the ladder leg) with the Mn-O-Mn bond angle of 125.26°. Mn–O–Mn bond angles larger than 110° usually induces antiferromagnetic couplings in Mn²⁺ polynuclear complexes.^{21b} Furthermore, the triatomic (-OCO-) syn-syn mode may induce more efficient antiferromagnetic coupling than other triatomic bridges, with the magnitude comparable to or even greater than the monatomic (-O-) bridge.²² Since the temperature dependence of the susceptibility has revealed that antiferromagnetic interaction dominates the magnetic property of 1, it is reasonable to consider the coupling along the ladder leg first. Thus, we can estimate the exchange interaction of this ladder-like chain by a following simple approach in which the ladder can be treated as the linkage of two uniform chains with intra-chain and inter-chain exchange constants. For the intra-chain antiferromagnetic interaction (J), we used the classical 1D uniform chain theoretical expression proposed by Fisher.23

$$\chi_{\text{chain}} = [N\beta^2 g^2 S(S+1)/3kT](1+u)/(1-u) \tag{1}$$

Where $u = \operatorname{coth}[JS(S + 1)/kT] - kT/JS(S + 1)$ and S = 5/2. The J parameter is based on the spin Hamiltonian $H = -2J\Sigma S_i \cdot S_{i+1}$ and the S operator is treated as a classical spin operator. The inter-chain interaction (zJ') through the rungs of the ladder was treated by the molecular field approximation²⁴

$$\chi_{\text{ladder}} = \chi_{\text{chain}} / [1 - 2z J' \chi_{\text{chain}} / N \beta^2 g^2]$$
(2)

Using this approximate model, the susceptibility data were simulated, giving the best fit in the whole temperature range with the parameters $J = -3.51 \text{ cm}^{-1}$, $zJ' = +0.22 \text{ cm}^{-1}$ and g = 1.94. The agreement factor $R = \Sigma (\chi_{obs} T - \chi_{calc} T)^2 / \Sigma (\chi_{obs} T)^2$ is 8.4×10^{-5} . The large negative J value is consistent with the magnetic coupling interactions observed in some Mn²⁺ carboxylate complexes bridged by the *syn–syn* and $\mu_3-\eta^2$ bridging carboxylate groups with larger Mn–O–Mn bond angles.^{22,25} While the inter-chain exchange pathway *zJ'* originates from two μ_2 -oxygen bridges together with two *syn–anti* carboxylate bridge usually transmits weak antiferromagnetic coupling interactions,²² which counteracts the ferromagnetic interactions *via* two μ_2 -oxygen bridges to some extent and leads to a comparatively small positive *zJ'* value.

Below 4 K and at an applied field of 0.01 T, the $\chi_m T$ product experiences an upturn, reaching 1.18 emu K mol⁻¹ at 2 K. When the applied field is larger than 0.1 T, the increasing tendency of the $\chi_m T$ product is inconspicuous and completely disappears at higher fields. Upon cooling, the χ_m value increases smoothly to a maximum at *ca.* 24.0 K and then decreases slightly. Below 5.5 K, a relatively abrupt increase, which is more obvious in lower magnetic fields, can be observed (Fig. 7, bottom). This low temperature field-dependent behaviour suggests the occurrence of very weak ferromagnetic interactions in **1**, which may arise from the presence of canting between the anti-parallel alignment of the spins.⁷

The canting behaviour in 1 can be confirmed by the M(H)curve, which has a fast increase of the magnetization at very low fields and a linear variation of M(H) at H > 0.065 T. The curve reaches a value of $0.81N\beta$ at 7 T and is far less than the saturated value of $5N\beta$ expected for an isolated Mn²⁺ ion (Fig. 8). This lack of saturation at high applied field is consistent with the presence of a spin-canted antiferromagnetic state. The hysteresis loop measured at 2 K shows values of the coercive field (H_c) and remnant magnetization (M_R) of 48.5 Oe and 0.0094 $N\beta$, respectively (the inset of Fig. 8), being characteristic of a soft magnet. The canting angle is estimated to be about 0.11° from the expression $\sin \alpha = M_{\rm R}/M_{\rm s}$.²⁶ In 1, the in-phase signal (χ_m') presents a maximum at *ca.* 3 K, whereas the out-of-phase signal (χ_m'') is not observed (ESI, Fig. S5).[†] The similar ac susceptibility behaviour has been reported for some Mn2+ and Co2+ complexes.²⁷ In all these magnetic entities the magnetic moment arising from canting is so small that the loss of energy related to the out-of-phase signal can be ignored. It is well known that the occurrence of spin canting is usually caused by either singleion magnetic anisotropy or antisymmetric exchange in magnetic entities.⁷ Due to the negligible single-ion anisotropy for highspin Mn²⁺,⁷ the observation of the spin canting in 1 should arise from the antisymmetric magnetic exchange, which is related to the antisymmetric nature of the magnetic entities. In 1, the antisymmetry of the ligand is transferred to the whole 3D structure to finally lead to a non-centrosymmetric space group *Iba2*, which is in the absence of an inversion center between the neighbouring Mn²⁺ ions and is low enough to allow the antisymmetric exchange coupling to operate. Such spin-canting effects arising from the antisymmetric exchange interaction have been observed in some isotropic Mn²⁺ and Fe³⁺ complexes.²⁸



Fig. 8 Field-dependent magnetization and hysteresis loop for 1 at 2.0 K.

The temperature dependence of the χ_m and $\chi_m T$ measured at 0.5 T for **2** is shown in Fig. 9 (χ_m being the magnetic susceptibility of two Mn²⁺ ions). The $\chi_m T$ value is about 8.79 emu K mol⁻¹ at room temperature, close to the expected value for two isolated octahedral Mn²⁺ ions (8.75 emu K mol⁻¹). From 300–40 K, there is a smooth decrease of the $\chi_m T$ value, while from 40–2 K, there is a sharp decline in $\chi_m T$, finally reaching 1.19 emu K mol⁻¹. The χ_m values show a small maximum at about 4.0 K, suggesting the occurrence of weak antiferromagnetic interactions between the two adjacent Mn²⁺ ions. Taking into account the dimer character in the structure of **2**, the $\chi_m T$ data were fitted by using the isotropic Heisenberg model $H = -2JS_1 \cdot S_2$ for two interacting S = 5/2 centers to determine the exchange parameters *via* a *syn–anti* carboxylate group.²⁹ The best fit is given in the whole temperature



Fig. 9 Temperature dependence of $\chi_m T$ product at 0.5 T for compound 2. The solid line corresponds to the best fit to a dimer model. The inset shows the temperature dependence of χ_m at different external fields in the range 0.1–4.5 T.

range with the super-exchange parameters J = -0.55 cm⁻¹, g = 2.04, and $R = 1.2 \times 10^{-4}$. These parameters agree with the *syn-anti* carboxylate-bridged dimer with a long Mn ··· Mn distance of 5.43 Å in **2** and are comparable to the observation in the compounds reported previously.^{22,29}

The comparison of χ_m vs. T curves at different magnetic fields from 0.1-4.5 T (the inset of Fig. 9), suggests that there is an obvious occurrence of a transition to an antiferromagnetic state at the lower field, with a maximum value at about 4.0 K. On the contrary, the maximum vanishes above 3 T, indicating that the transition is suppressed at higher magnetic fields. Furthermore, isothermal magnetization curves at T = 2 and 3.5 K in the applied field 0–7 T (Fig. 10) reveal that the magnetization reaches $9.1N\beta$ at 2 K and $8.5N\beta$ at 3.5 K with the highest applied field, which are all less than the expected saturation value of $10N\beta$ for two isolated Mn²⁺ ions. The sigmoidal shape of the M(H) dependence as shown in Fig. 10 and the disappearance of the χ_m maximum at higher fields suggest the occurrence of a field-induced magnetic transition. This field-independent magnetic behaviour is characteristic of a spin-flop transition, which often occurs in antiferromagnets with small anisotropy.⁷ The transition field, determined by a dM/dHderivative curve, is ca. 3.2 T at 2 K (the inset in Fig. 10).



Fig. 10 Magnetization curves at 2 and 3.5 K in the applied field range 0-7 T for 2. The inset shows the derivative of the isothermal magnetization with respect to dc field at 2 and 3.5 K.

Plots of the $\chi_m T$ and χ_m^{-1} vs. *T* for **3** are shown in Fig. 11. The $\chi_m T$ value of 8.73 emu K mol⁻¹ at room temperature is close to that expected for two non-interacting high-spin Mn²⁺ ions. As the temperature is lowered from 300–50 K, there is a smooth decrease in the $\chi_m T$ value, whereas below 50 K, the $\chi_m T$ value decreases sharply and reaches 2.08 emu K mol⁻¹ at 2 K. The magnetic susceptibility data can be fitted to the Curie–Weiss law in the whole temperature with $\theta = -9.5$ K, indicating dominant



Fig. 11 Temperature dependence of the $\chi_m T$ product and χ_m^{-1} of **3** at 0.5 T, the solid lines represent the Curie–Weiss fit. The inset shows the isothermal magnetization curve at 2 K.

antiferromagnetic interactions in **3**. The isothermal magnetization curve at 2 K is far from saturation, reaching 5.6 $N\beta$ per Mn₂ unit at 6 T, which is less than the expected saturation value of 10 $N\beta$ for two isolated Mn²⁺ ions with S = 5/2 and g = 2, consistent with the presence of antiferromagnetic interactions (the inset in Fig. 11).

From a magnetic topology view point, the 1D $[Mn(CO_2)_2]_n$ chain in **3** can be considered as an alternating chain with two sets of repeat exchange pathways (--- J_1 --- J_2 --- J_2 ---): one consists of two *syn–syn* carboxylate bridges and one μ_2 -O bridge from the μ_3 -carboxylate group with the Mn1–O16–Mn2 angle of 103.36° (J_1); the other includes one *syn–syn* carboxylate bridge and one μ_2 -O bridge from the μ_3 -carboxylate group with the Mn2– O15–Mn3 angle of 114.88° (J_2). Due to the presence of the μ_3 carboxylate bridge, the *syn–anti* carboxylate bridges may make an additional contribution to both the J_1 and J_2 exchange pathways. Except the μ_2 -O bridge with a Mn–O–Mn angle of 103.36°, which may show weak ferromagnetic^{21a} or antiferromagnetic coupling interactions,³⁰ all other bridging modes may induce antiferromagnetic couplings in Mn²⁺ complexes.²² Therefore, the dominant antiferromagnetic interaction observed in **3** is reasonable.

Conclusions

In conclusion, by utilizing an unsymmetrical carboxylic acid ligand, three novel molecule-based magnetic coordination polymers have been successfully synthesized and structurally characterized. It is interesting to note that a novel 3D acentric coordination network containing carboxylate-bridged 1D ladder-like manganese chains can be obtained in the absence of co-ligands, whereas the centrosymmetric compounds 2 and 3 were obtained in the presence of 2,2'-bpy or 4,4'-bpy. All three compounds exhibit dominant antiferromagnetic interactions. Compound 1 shows a spin-canted magnetic property, which may arise from the antisymmetric magnetic exchange interaction, whereas compound 2 is a weak antiferromagnet, which exhibits a field-induced spin-flop magnetic transition at *ca.* 3.2 T at 2 K.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20671090/50372069), the Natural Science Foundation of Fujian Province of China (No. E0220003), and Key Project from CAS (KJCX2-YW-H01). The authors sincerely thank Prof. Song Gao and Dr Bing-Wu Wang for their help in simulating the magnetic data of compound **1**.

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