Crystal structures and magnetic properties of two- and three-dimensional malonato-bridged manganese(II) complexes

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Two new manganese(II) compounds of formula $[Mn(mal)(H_2O)(2,4'\text{-bpy})]_n$ (**1**) and $[Mn_2(mal)_2(H_2O)_2(4,4'\text{-bpy})]_n$ (**2**) ($2,4'$-bpy = 2,4′-bipyridine, $4,4'$-bpy = 4,4′-bipyridine and H_2mal = malonic acid) have been prepared and structurally characterized by X-ray crystallography. Their structures are made up of two- (**1**) and three-dimensional (**2**) arrangements of manganese atoms linked by carboxylate-malonate groups in the *anti–syn* bridging mode (**1** and **2**) and bis(monodentate) 4,4′-bpy (**2**). The 2,4′-bpy group in **1** acts as a monodentate ligand. Each manganese atom in **1** and **2** is six-coordinated with four carboxylate-oxygens in the equatorial plane and a nitrogen atom and a water molecule in the axial positions. The magnetic properties of **1** and **2** and those of the related sheet-like polymer $[Mn(mal)(H_2O)_2]_n$ (**3**) (whose structure was published elsewhere, orthorhombic $Pca2_1$) have been investigated in the temperature range 2.0–290 K. The magnetic coupling between the manganese(II) ions in **1** and **2** through the single carboxylato bridge is weakly antiferromagnetic and practically identical (J $ca.$ -0.2 cm^{-1}). Weak antiferromagnetic coupling is also observed in complex **3** (occurrence of carboxylate bridges in the *anti–anti* and *anti–syn* bridging modes) together with spin canting behaviour at very low temperatures (T_c = 2.7 K). The antisymmetric exchange is most likely responsible for the small canting observed in **3**.

Introduction

The study of molecule-based magnets is an emerging area of contemporary materials research.[1] Judicious choice of appropriate molecular building blocks provides the means to create a rich variety of new materials with interesting structural and magnetic properties. Typically, these compounds consist of paramagnetic transition metal ions linked together by organic ligands of various sizes, shapes, and bonding motifs to afford one-, two-, and three-dimensional (nD with $n = 1$–3) arrays. A great deal of modern literature describes compounds containing cyano,[2] oxalato,[3] azido,[4] or dicyanamide[5] as bridges which offer a great variety of magnetic behaviours issuing from the ferro- or antiferro-magnetic interactions between the paramagnetic centres they link.

We have chosen the flexible malonate ligand, $^-OOC–CH_2–COO^-$, to develop a wide range of architectures which exhibit magnetic coupling. The occurrence of two carboxylate groups in 1,3 positions allows this ligand to adopt simultaneously chelating bidentate and different carboxylato bridging modes (*syn–syn, syn–anti* and *anti–anti*) through one or both carboxylate groups.[6–13] The ability of the carboxylato bridge to mediate significant ferro- or antiferro-magnetic interactions[14–18] between the paramagnetic metal ions it bridges, enhances the interest in the malonato ligand aimed at designing extended magnetic systems. Combining the malonate with ancillary ligands, such as pyrazine (pyz), 2,4′-bipyridine (2,4′-bpy), 4,4′-bipyridine (4,4′-bpy), and 2,2′-bipyridine (2,2′-bpy) we have been able to prepare compounds of formula $[Cu_4(mal)_4(2,4\text{-bpy})_4]\cdot8H_2O$ (tetranuclear), $[Cu_2(mal)(H_2O)_2(2,2'\text{-bpy})](ClO_4)_2$ (1D), $[Cu_4(mal)_4(H_2O)_4(4,4'\text{-bpy})_2]$ (2D) and $[Cu_4(mal)_4(pyz)_2]\cdot4H_2O$ (3D).[19–21] One of the most interesting aspects of all these malonato-copper(II) complexes is the ferromagnetic coupling that takes place through the carboxylato-malonate bridge.[19–21]

Mn(II) with azido or dicyanamide ligands generates one-,[4a,l] two-[4j,k] and three-dimensional[4i,5a–c] networks, exhibiting in general antiferromagnetic coupling, some of them behaving as weak ferromagnets.[4i,j,5a,c]

In this context and following our systematic studies on malonato-containing metal complexes,[19–22] we present here the preparation and magneto-structural investigation of the manganese(II) complexes $[Mn(mal)(H_2O)(2,4'\text{-bpy})]_n$ (**1**) and $[Mn_2(mal)_2(H_2O)_2(4,4'\text{-bpy})]_n$ (**2**) (H_2mal = malonic acid), which are two- (**1**) and three-dimensional (**2**) compounds. The magnetic behaviour of the related sheet-like polymer $[Mn(mal)(H_2O)_2]_n$ (whose structure was published elsewhere)[23] is also included for comparison.

Results and discussion

Crystal structures

Description of the structure of $[Mn(mal)(H_2O)(2,4'\text{-bpy})]_n$ (1). Compound **1** has a sheet-like arrangement of *trans*-aqua(2,4′-bipyridine)manganese(II) units bridged by malonate ligands (Fig. 1). Each malonate group is coordinated to a manganese atom as a bidentate ligand through two oxygen atoms of the two carboxylate fragments [O(1) and O(3)] and it is also coordinated to two other neighbouring manganese atoms in a bis(monodentate) fashion through the free carboxylate-oxygens [O(2) and O(4)] toward Mn(1c) and Mn(1d), respectively; symmetry codes: (c) = $x + 1/2$, $y + 1/2$, $-z + 3/2$ and (d) = $x - 1/2$, $y + 1/2$, $-z + 3/2$]. A corrugated square grid of manganese atoms which is perpendicular to the c axis results where the 2,4′-bpy terminal ligands are alternatively located above and below each layer (Fig. 2a). The manganese atom exhibits a slightly distorted octahedral environment (Fig. 3a): two carboxylate-oxygen atoms [O(1) and (3)] from a bidentate malonate
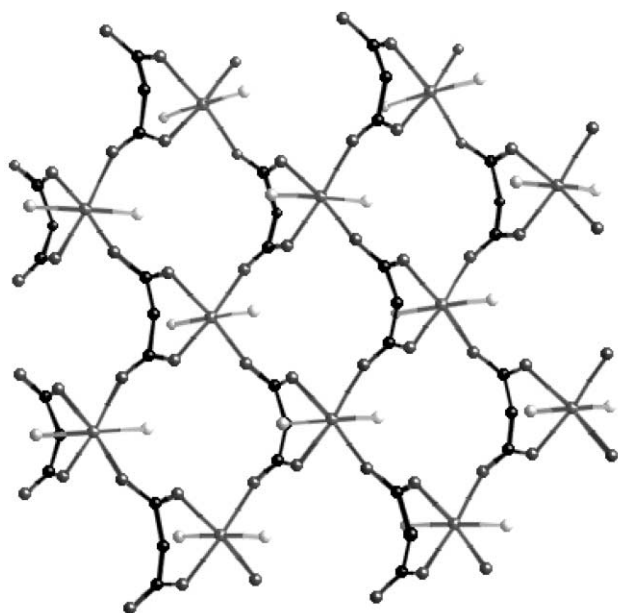
Fig. 1 A view of a fragment of a corrugated layer of [Mn(mal)-(H$_2$O)(2,4′-bpy)]$_n$ (**1**). The atoms of 2,4′-bpy ligands have been omitted for clarity. The layers are almost equal to those of [Mn$_2$(mal)$_2$-(H$_2$O)$_2$(4,4′-bpy)]$_n$ (**2**).

and two other carboxylate oxygen atoms [O(2a) and O(4b); (a) = $x − 1/2$, $y − 1/2$, $−z + 3/2$ and (b) = $x + 1/2$, $y − 1/2$, $−z + 3/2$] from two adjacent malonate ligands in the equatorial positions, and a water molecule [O(1w)] and a nitrogen atom [N(1)] from the 2,4′-bpy ligand in the axial positions describe a six-coordinated MnNO$_5$ unit. The distortion of the manganese octahedron can be adequately described by the degree of compression (s/h) and the twisting angle (ϕ), these values being 1.24 and 57.37° respectively ($s/h = 1.22$ and $\phi = 60°$ in a perfect octahedron),[24] selected bond distances and angles for **1** are shown in Table 1.

Each malonate ligand has an envelope conformation and it forms a six-membered chelate ring at the manganese atom, the value of the angle subtended at the metal atom being 83.5(3)°. The carboxylate groups adopt the *anti–syn* coordination mode, the value of the Mn · · · Mn separation through this bridge being 5.514(10) Å, a value which is much shorter than the shortest interlayer Mn · · · Mn separation [*ca.* 13.204(10) Å]. The malonate oxygen atoms contribute to the stabilization of the crystal structure through hydrogen bonding involving the coordinated water molecule [2.786(17), 3.156(14), 2.603(19) and 3.081(15) Å for O(1w) · · · O(1a), O(1w) · · · O(2a), O(1w) · · · O(3b) and O(1w) · · · O(4b), respectively]. Weaker C–H(2,4′-bpy) · · · O(mal) type interactions are also observed [3.302(23), 3.379(24) and 3.112(17) Å for C(11) · · · O(1), C(11) · · · O(3) and C(12) · · · O(2a), respectively].

The pyridyl rings of the 2,4′-bpy are planar but the ligand as a whole is far from being planar [the dihedral angle between the two pyridyl rings is 29.39(12)°]. The shortest distance between two 2,4′-bpy ligands is 4.232(11) Å indicating weak π–π stacking interactions. The mean C–C distances [1.510(22) Å] are longer than those reported for other Mn(II)–2,4′-bpy complexes [1.486 Å].[25a,b]

Description of the structure of [Mn$_2$(mal)$_2$(H$_2$O)$_2$(4,4′-bpy)]$_n$ (2). The structure of **2** consists of a three-dimensional arrangement of (aqua)manganese(II) units bridged by malonate and 4,4′-bpy ligands (Fig. 2b). The simplest way to describe this structure is as corrugated layers of malonato-bridged manganese atoms growing in the *ab* plane which are linked through bis(monodentate) 4,4′-bpy to afford the three-dimensional network. The arrangement of the atoms in each layer is very similar to that of **1**, the carboxylate group in **2** exhibiting also
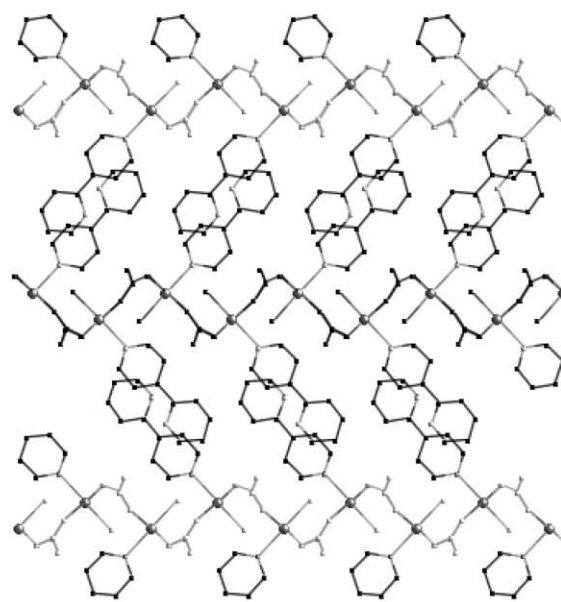
(a)
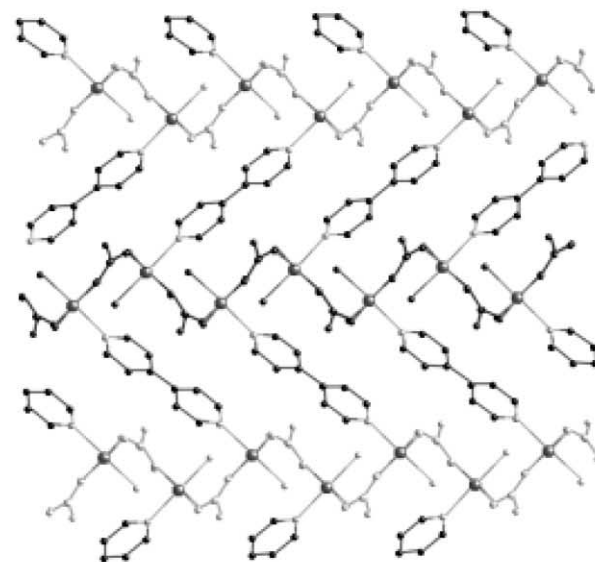
(b)

Fig. 2 (a) Projection of layers of [Mn(mal)(H$_2$O)(2,4′-bpy)]$_n$ (**1**) down the *a* axis. (b) Projection of [Mn$_2$(mal)$_2$(H$_2$O)$_2$(4,4′-bpy)]$_n$ (**2**) down the *c* axis showing the parallel layers and their cross-linking through the 4,4′-bpy ligand.

the *anti–syn* bridging mode. The main difference between **1** and **2** is the bridging character of the 4,4′-bpy in **2** *versus* the blocking one of the 2,4′-bpy molecules (terminally bound ligand) in **1**.

As in **1**, the manganese atom is six-coordinated with four oxygen atoms of three different malonate ligands filling the equatorial positions and a water molecule and one nitrogen atom from the 4,4′-bpy in the axial ones (Fig. 3b). The distortion of the manganese octahedron is $\phi = 58.59°$ and $s/h = 1.18$. The selected average bond distances and angles are reported in Table 1.

The bis(monodentate) 4,4′-bpy ligands are alternatively located above and below the network plane linking manganese atoms of neighbouring layers [Mn · · · Mn interlayer distance of 11.632(2) Å], the bridging 4,4′-bpy molecules enclosing void channels of minimum atom–atom cross-section of 10.973(4) ×

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

Compound **1**				Compound **2**			
Mn(1)–O(1)	2.149(13)	Mn(1)–O(4b)	2.157(11)	Mn(1)–O(1)	2.167(3)	Mn(1)–O(4)	2.168(3)
Mn(1)–O(2a)	2.176(11)	Mn(1)–O(1W)	2.247(6)	Mn(1)–O(2)	2.164(3)	Mn(1)–O(1W)	2.235(2)
Mn(1)–O(3)	2.217(11)	Mn(1)–N(1)	2.257(9)	Mn(1)–O(3)	2.171(3)	Mn(1)–N(1)	2.276(2)
O(1)–Mn(1)–O(2a)	171.1(4)	O(3)–Mn(1)–O(1W)	92.4(5)	O(1)–Mn(1)–O(2)	168.35(12)	O(3)–Mn(1)–O(1W)	92.13(10)
O(1)–Mn(1)–O(3)	83.5(3)	O(3)–Mn(1)–N(1)	88.3(8)	O(1)–Mn(1)–O(3)	82.90(11)	O(3)–Mn(1)–N(1)	93.11(10)
O(1)–Mn(1)–O(4b)	92.9(4)	O(4b)–Mn(1)–O(1W)	88.8(5)	O(1)–Mn(1)–O(4)	89.29(12)	O(4f)–Mn(1)–O(1W)	88.04(10)
O(1)–Mn(1)–O(1W)	91.7(5)	O(4b)–Mn(1)–N(1)	90.6(8)	O(1)–Mn(1)–O(1W)	90.20(11)	O(4f)–Mn(1)–N(1)	86.21(10)
O(1)–Mn(1)–N(1)	89.0(8)	O(1W)–Mn(1)–N(1)	179.1(3)	O(1)–Mn(1)–O(N1)	86.33(10)	O(1W)–Mn(1)–N(1)	173.31(10)
O(2a)–Mn(1)–O(3)	87.9(5)	Mn(1)–O(1)–C(1)	132.0(12)	O(2)–Mn(1)–O(3)	85.75(11)	Mn(1)–O(1)–C(1)	129.6(2)
O(2a)–Mn(1)–O(4b)	95.7(3)	Mn(1)–O(2a)–C(1a)	131.1(10)	O(2)–Mn(1)–O(4)	102.04(12)	Mn(1)–O(2)–C(1e)	127.9(3)
O(2a)–Mn(1)–O(1W)	90.7(5)	Mn(1)–O(3)–C(3)	121.6(11)	O(2)–Mn(1)–O(1W)	92.87(10)	Mn(1)–O(3)–C(3)	129.4(2)
O(2a)–Mn(1)–N(1)	88.7(8)	Mn(1)–O(4b)–C(3b)	131.6(10)	O(2)–Mn(1)–N(1)	91.67(9)	Mn(1)–O(4)–C(3f)	132.5(3)
O(3)–Mn(1)–O(4b)	176.2(5)			O(3)–Mn(1)–O(4)	172.19(11)		

Symmetry code: a = $x - 1/2, y - 1/2, -z + 3/2$; b = $x + 1/2, y - 1/2, -z + 3/2$; .e = $x + 1/2, -y + 1/2, z + 1/2$; f = $x + 1/2, -y + 1/2, z - 1/2$.
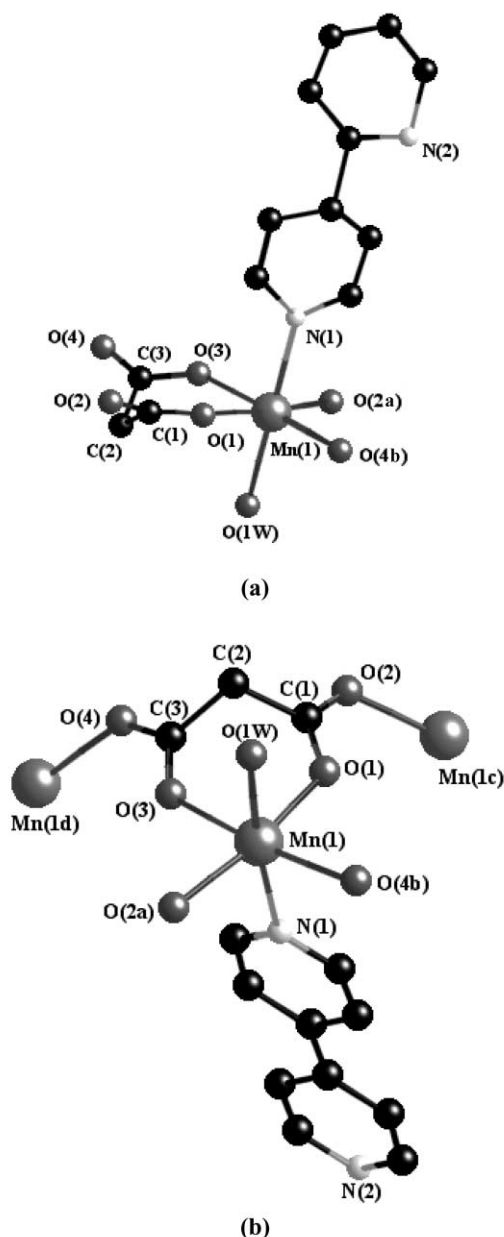
Fig. 3 Coordination geometry of the manganese atom in [Mn(mal)-(H$_2$O)(2,4′-bpy)]$_n$ (**1**) (a) and [Mn$_2$(mal)$_2$(H$_2$O)$_2$(4,4′-bpy)]$_n$ (**2**) (b).

11.632(2) Å along the *a* axes. The pyridyl rings of the 4,4′-bpy are planar and the ligand as a whole is also planar. Bond lengths and angles within the 4,4′-bipy are in agreement with those reported for this ligand in structurally characterized 4,4′-bpy-bridged manganese(II) compounds.[25c-e]

Each malonate ligand has an envelope conformation and it forms a six-membered chelate ring at the manganese atom. The carboxylate groups adopt the *anti–syn* coordination mode, the value of the Mn(1) ⋯ Mn(1h) [(h) = $x - 1/2, -y + 1/2, z + 1/2$] separation through this bridge being 5.413(4) Å, a value which is much shorter than the shortest interlayer Mn ⋯ Mn separation [*ca.* 11.632(6) Å]. The malonate ligand adopts simultaneously bidentate [through O(2) towards Mn(1g) and through O(4) towards Mn(1h); (g) = $x - 1/2, -y + 1/2, z - 1/2$].

There is an intricate O(W) ⋯ O(malonate) hydrogen bonding network involving the coordinated water molecules [O(1W)] and the four oxygens of the malonate anions [the mean distance being 2.707(4), 3.188(4), 2.720(4) and 3.060(4) Å for O(1W) ⋯ O(1e), O(1W) ⋯ O(2e), O(1W) ⋯ O(3f) and O(1W) ⋯ O(4f), respectively; (e) = $x + 1/2, -y + 1/2, z + 1/2$ and (f) = $x + 1/2, -y + 1/2, z - 1/2$].

Description of the structure of [Mn(mal)(H$_2$O)]$_n$ (3). The structure of **3** was previously described by Lis *et. al.*[23] and it consists basically of layers of *trans*-diaquamanganese(II) units bridged by carboxylate-malonate groups in the *anti–anti* and *anti–syn* coordination modes (Fig. 4). Four carboxylate-oxygens [O(1), O(3), O(2k) and O(2l)]; (k) = $x, 1 - y, z - 1/2$ and (l) = $x, -y, z - 1/2$] from three malonate ligands fill the equatorial positions. In addition to the presence of carboxylate bridges in the *anti–anti* coordination mode, another important difference in **3** with respect to **1** and **2** is the high planarity of the layers and the very short interlayer Mn ⋯ Mn distance [5.380(6) Å]. The Mn ⋯ Mn separations through the *anti–anti* [Mn(1) ⋯ Mn(1j); (j) = $x, 1 - y, z + 1/2$] and *anti–syn* [Mn(1) ⋯ Mn(1i); (i) = $x, -y, z + 1/2$] carboxylate bridges are 5.790(4) and 6.319(4) Å, respectively. An extensive network of hydrogen bonds involving the coordinated water molecules and some of the malonate-oxygen atoms takes place.[23]

Magnetic properties of 1–3

Complexes 1 and 2. Plots of the molar magnetic susceptibility (χ_M) and the $\chi_M T$ product *vs. T* for **1** are shown in Fig. 5a. At room temperature, $\chi_M T$ is equal to 4.34 cm³ mol⁻¹ K, a value which is as expected for a magnetically isolated spin sextuplet ($\chi_M T$ = 4.375 cm³ mol⁻¹ K with g = 2.00). Upon cooling $\chi_M T$ continuously decreases to reach a value of 1.38 cm³ mol⁻¹ K at 2 K. This behaviour is indicative of the occurrence of weak antiferromagnetic interactions. The susceptibility plot does not exhibit any maximum in the temperature range studied, although an incipient maximum seems to be reached around 2.0 K.

Given that the structure of **1** is made of isolated square layers of Mn(II) ions, the bridge being the carboxylate-malonate in the
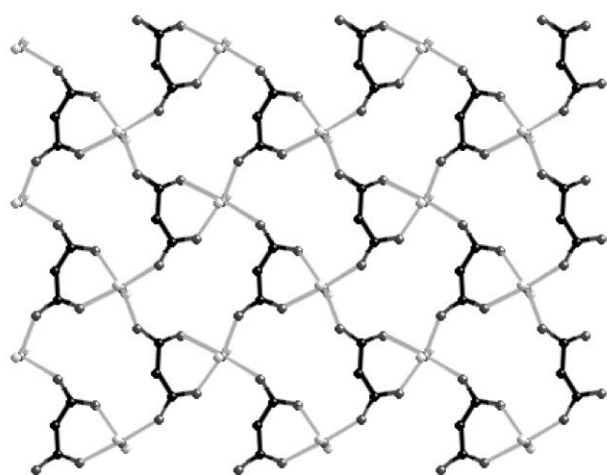
(a)
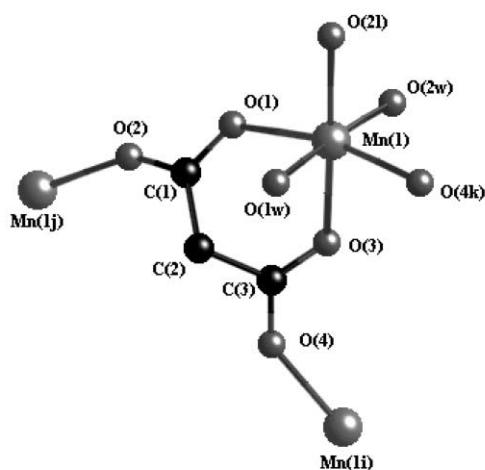
(b)

Fig. 4 (a) Lamellar structure of compound [Mn(mal)(H$_2$O)$_2$]$_n$ (**3**). (b) Coordination geometry of the manganese atom in [Mn(mal)(H$_2$O)$_2$]$_n$ (**3**).

anti–syn bridging mode, its magnetic behaviour can be analyzed through the expression derived by Lines for a S = 5/2 antiferromagnetic quadratic layer[26]

$$\frac{Ng^2\beta^2}{\chi|J|} = 3\theta + \left(\sum_{n=1}^{6} C_n/\theta^{n-1}\right) \qquad (1)$$

where $\theta = kT/|J|S(S + 1)$, C_1 = 4, C_2 = 1.448, C_3 = 0.228, C_4 = 0.262, C_5 = 0.119, C_6 = 0.017 and N, g, and β, have their usual meanings. The best least-squares fit parameters are J = −0.190(1) cm^{-1}, g = 2.007(1) and R = 2.0 × 10^{-5} [R is the agreement factor defined as $\Sigma_i[(\chi_M)\text{obs}(i) - (\chi_M)\text{calc}(i)]^2/\Sigma_i[(\chi_M)\text{obs}(i)]^2$]. The calculated curves (solid lines in Fig. 5a) match very well the experimental data.

Complex **2** exhibits a magnetic behaviour very similar to that of **1** (Fig. 5b): $\chi_M T$ is equal to 4.38 cm^3 mol^{-1} K at room temperature, and it decreases continuously upon cooling. Although **2** has a three-dimensional structure built up of Mn(II) malonate planes linked by the 4,4′-bpy, the magnetic coupling through the 4,4′-bpy seems to be very weak (metal ions separated by more than 11 Å, and most likely negligible compared to that through the *anti–syn* carboxylate bridge).[21] Consequently, the model we have used to analyze the magnetic properties of **1** is also valid for **2**.

The best fit parameters are J = −0.188(1) cm^{-1}, g = 2.013(1), and R = 3.0 × 10^{-7}. The calculated curves (solid lines in Fig. 5b)
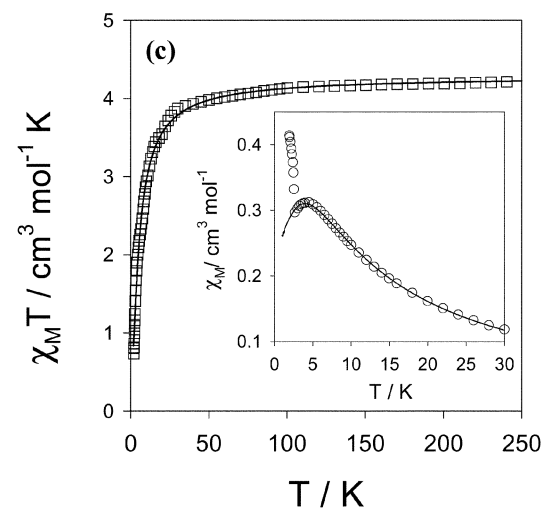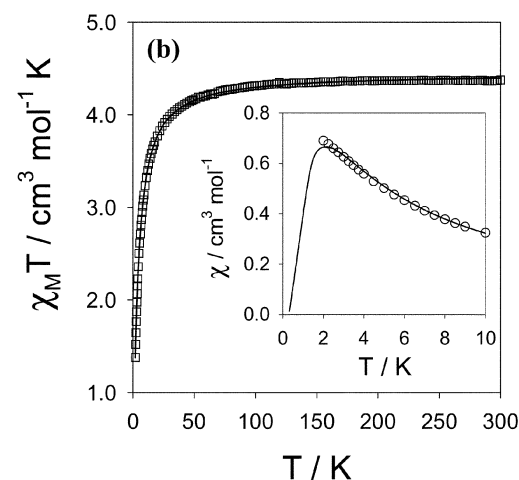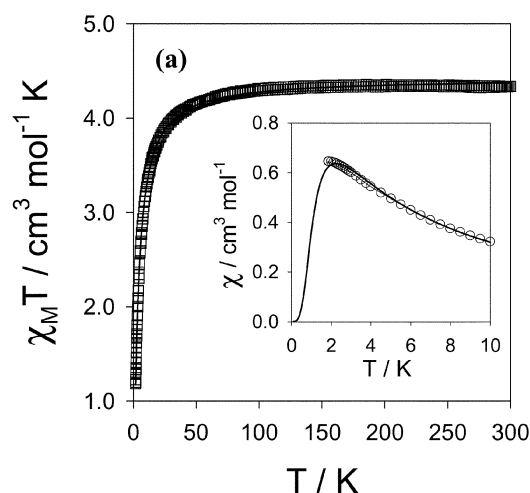

Fig. 5 Experimental (□) and calculated (——) variations of the $\chi_M T$ *vs.* T [χ_M is the magnetic susceptibility per Mn(II) ion] for [Mn(mal)(H$_2$O)(2,4′-bpy)]$_n$ (**1**) (a), [Mn$_2$(mal)$_2$(H$_2$O)$_2$(4,4′-bpy)]$_n$ (**2**) (b) and [Mn(mal)(H$_2$O)$_2$]$_n$ (**3**) (c). The insert shows the variation of the experimental (○) and calculated (——) molar magnetic susceptibility at low temperatures.

match very well the experimental data. The values of the intralayer antiferromagnetic coupling in **1** and **2** are practically identical as expected due to the identical carboxylate bridging mode involved.

Magneto-structural studies on polynuclear Mn(II) complexes containing carboxylato bridges have revealed the occurrence of weak antiferromagnetic couplings with J values of −0.19 cm^{-1} through a single bridge and in the ranges from −0.9 to −1.7 cm^{-1} and −3.5 to −4.4 cm^{-1} through the double and triple carboxylate bridges, respectively.[27] As the Mn(II) ions in **1**

and **2** are linked through a single bridge, the computed *J* values obtained being in agreement with the reported ones. The large Mn ⋯ Mn interlayer separation [13.204(10) and 11.632(6) Å for **1** and **2**, respectively] makes the interaction through the layers negligible, thus providing good examples of local *S* = 5/2 two-dimensional antiferromagnetic systems.

Complex 3. The $\chi_M T$ *vs. T* plot for compound **3** is shown in Fig. 5c. At room temperature, $\chi_M T$ is equal to 4.30 cm³ mol⁻¹ K. $\chi_M T$ smoothly decreases when cooling, and below 100 K it decreases more rapidly. The susceptibility curve (see insert of Fig. 5c) shows a maximum at 4.3 K, and an abrupt increase below 3 K. This susceptibility increase in the very low temperature range is most likely due to a spin canted structure (see below).

The structure of **3** is made of planar layers where the manganese(II) ions are bridged by carboxylate groups exhibiting alternating *anti–anti* and *anti–syn* coordination modes. Although both conformations are able to mediate significant magnetic coupling among paramagnetic centres, the latter gives much weaker interactions than the former.[18e,d,22c] Under this approach, and under a magnetic point of view, **3** can be described as *anti–anti* carboxylate-bridged manganese(II) chains linked through *anti–syn* carboxylate groups (see Scheme 1). Having this in mind we have analyzed the magnetic properties of **3** for *T* > 3 K through the Fisher[28] expression [eqn. (2)] for a chain of interacting spins *S* = 5/2

$$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT}\left[\frac{1+u}{1-u}\right] \quad (2)$$

with

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right] \quad (3)$$
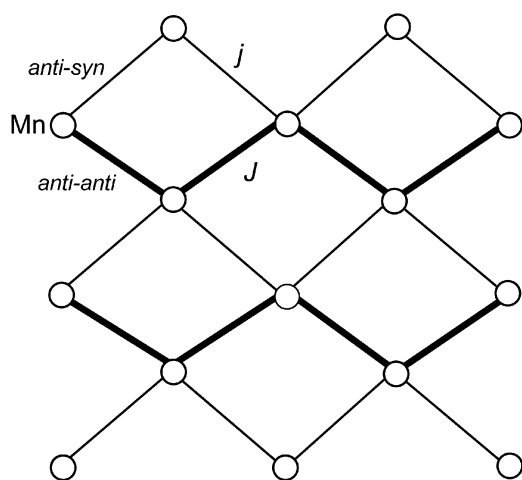
Scheme 1

An additional mean field correction term [$\theta = zjS(S+1)/3k$] is introduced (as *T* − *θ*) to consider the interchain interactions. The best least-squares fit parameters are *J* = −0.64(1) cm⁻¹, *g* = 1.99(2), *θ* = −0.0064(2) K and *R* = 2.2 × 10⁻⁵. The theoretical curve matches very well the experimental data up to 3 K (Fig. 5c). The magnitude of the exchange coupling *J* (interaction through the *anti–anti* carboxylate bridge) in **3** is greater than those of compounds **1** and **2**, in which the carboxylate exhibited only the *anti–syn* conformation. One can see that as far as the magnetic coupling is concerned, the number of bridges is not the only factor to be considered, but also their conformation. Nevertheless, the value obtained is lower than that reported for the double carboxylate bridge.[27] The value

obtained for the interchain magnetic interaction from the Weiss constant is *j* = −0.0075 cm⁻¹. This value is too small when compared to those obtained for compounds **1** and **2** where the same conformation of the carboxylate was involved. This difference is due to the fact that the value of *j* in **3** is underestimated: due to the spin canting, only the magnetic data above 3 K were considered in the fit and the influence of the very low temperature magnetic data on the value of *θ* is very important.

Below 2.7 K the magnetic susceptibility increases abruptly deviating from the theoretical curve (Fig. 5c). This behaviour is characteristic of a spontaneous moment due to spin canting, the compound exhibiting a long range magnetic ordering as confirmed by the field-cooled (FC) and the zero-field-cooled (ZFC) magnetisation plots (Fig. 6). The FC magnetization curve shows an abrupt increase at *T* below 2.8 K, and tends to saturation at lower temperatures. The ZFC magnetization curve increases as temperature is increased displaying a maximum value at *T* = 2.6 K, and at *T* = 2.75 K its value coincides with the value of the FC curve. From these experiments the order temperature can be stated as 2.7(1) K. Further information on the three-dimensional ordering is provided by the temperature dependence of the ac magnetic susceptibility measurements[29] (see insert of Fig. 6). The out-of-phase magnetic susceptibility, χ'', has a non-zero value below 2.8 K and a maximum value at 2.7 K. The ac measurements which were performed in the 100 to 1500 Hz frequency range show no frequency dependence. From the dc and ac magnetic measurements the value of T_c was determined as 2.7(1) K.
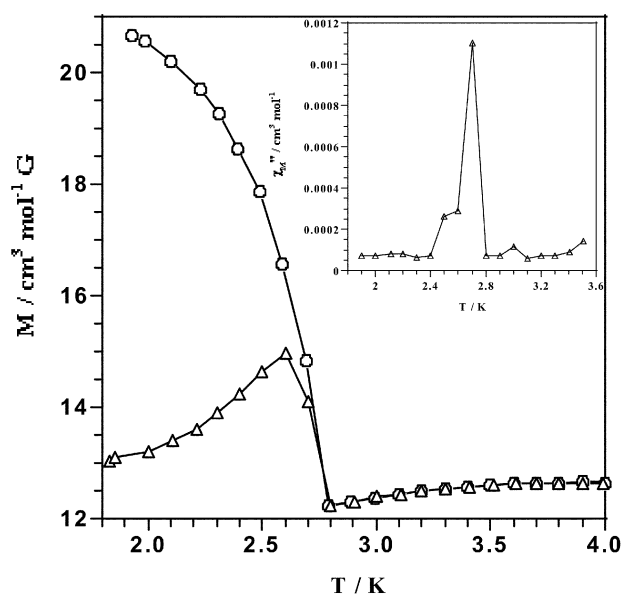
Fig. 6 Zero-field cooled (△) and field-cooled magnetisation (○) as a function of the temperature for [Mn(mal)(H₂O)₂]ₙ (**3**). The solid line is an eye-guide. The insert shows the temperature dependence of the out-of-phase ac susceptibility, χ'', for **3**, measured in an oscillatory field of 1 G and at 333 Hz.

The spin canting can arise from (a) single-ion local anisotropy and/or (b) antisymmetric exchange.[30] Given that six-coordinated Mn(II) has a ⁶A₁g ground state (state with a high isotropic character), the antisymmetric exchange must be responsible for the spin canting observed in **3**. The acentric character of the space group of **3** accounts for the occurrence of a spin canted structure for this compound through the antisymmetric exchange. In the case of complex **2**, the centrosymmetric character of its structure precludes the occurrence of spin canting. Finally, in the case of complex **1**, because of the presence of symmetry planes in the *b* and *c* axes, an inversion centre in the midpoint of each of three manganese atoms occurs and this rules out the spin canting situation.

Conclusions

The *anti–syn* carboxylate bridge mediates weak antiferromagnetic interactions in compounds **1** and **2** and these compounds behave as antiferromagnets. The strongest antiferromagnetic coupling has been found for compound **3**, for which a magnetic ordering is observed at very low temperature (T_c = 2.7 K). Spin canting through antisymmetric exchange is responsible for the magnetic ordering in **3** whereas this mechanism is forbidden for **1** and **2** due to symmetry reasons.

Experimental

Materials

Manganese(II) acetate tetrahydrate (from Merck); malonic acid, 2,4′-bipyridine hydrate and 4,4′-bipyridine (from Aldrich) were used as received. Elemental analyses (C, H, N) were performed on a EA 1108 CHNS-O microanalytical analyzer.

Synthesis of the complexes

[Mn(mal)(H₂O)(2,4′-bpy)]$_n$ (1). Single crystals suitable for X-ray diffraction were obtained by slow diffusion in an H-tube of two solutions containing manganese(II) acetate (2.5 mmol, 0.610 g) and malonic acid (2.5 mmol, 0.260 g) in one arm and 2,4′-bpy (2.5 mmol, 0.435 g) dissolved in a 50 : 50 ethanol–water mixture in the other. The light yellow crystals were collected, air dried and used for all the measurements (yield *ca.* 65%). Elemental analysis found: C, 47.46; H, 3.27; N, 8.65. Calc. for $C_{13}H_{12}N_2O_5Mn$ (**1**): C, 47.15; H, 3.65; N, 8.46%. IR (KBr, cm^{-1}) ν_{as}(COO) 1625s, 1575vs, ν_s(COO) 1443m, 1338s, ν(2,4′-bpy) 1609m, 1414m.

[Mn₂(mal)₂(H₂O)₂(4,4′-bpy)]$_n$ (2). Single crystals of **2** were obtained similarly to those of **1**, using 4,4′-bpy in instead of 2,4′-bpy (yield *ca.* 68%). Elemental analysis found: C, 36,76; H, 3.14; N, 5.58. Calc. for $C_{16}H_{16}N_2O_{10}Mn_2$ (**2**): C, 37.96; H, 3.19; N, 5.53%. IR (KBr, cm^{-1}) ν_{as}(COO) 1625s, 1574vs, ν_s(COO) 1447m, 1349s, ν(4,4′-bpy) 1608m, 1416m.

[Mn(H₂O)₂(mal)]$_n$ (3). Was prepared by the reaction of an aqueous solution (15 ml) of manganese(II) acetate (8 mmol, 1.96 g) with another solution (10 ml) of malonic acid (8 mmol, 0.823 g) in a steam bath for 20 min. A white precipitate was formed that was collected by filtration and washed with water and ethanol and dried with diethyl ether (yield *ca.* 95%). Light-yellow single crystals suitable for X-ray diffraction and magnetic measurements were obtained by recrystallisation from water of the white precipitate. Elemental analysis found: C, 18.76; H, 3.05. Calc. for $C_3H_6O_6Mn$ (**3**): C, 18.66; H, 3.11%. IR (KBr, cm^{-1}) ν_{as}(COO) 1669s, 1570vs; ν_s(COO) 1449m, 1380s, 1284m; δ(OCO) 811m, 722m.

Physical techniques

IR spectra (450–4000 cm^{-1}) were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 2.0–290 K with a Quantum Design SQUID magnetometer. The dc measurements were performed with an applied field of 100 G for T < 10 K and 1000 G for T > 10 K. The zero-field cooled magnetisation (ZFCM) measurements were performed cooling the sample in zero-field and then applying a field of 50 G, performing the data acquisition upon warming. The field-cooled magnetisation measurements (FCM) were performed acquiring the data cooling in an applied field of 50 G. The ac measurements were performed in a zero-field cooled sample then applying a variable field of 1–3 G in the range 100–1500 Hz. Diamagnetic corrections of the constituent atoms were estimated from

Table 2 Crystal data and structure determination summary for complexes **1** and **2**

	1	2
Chemical formula	$C_{13}H_{12}N_2O_5Mn$	$C_{16}H_{16}N_2O_{10}Mn_2$
Formula weight	331.2	506.2
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_1cn$	$P2_1/n$
a/Å	7.254(1)	7.291(2)
b/Å	7.727(1)	18.454(3)
c/Å	24.413(1)	7.532(2)
β/°	–	91.68(3)
V/Å³	1368.4(3)	1013.0 (4)
Z	4	4
D_{calc}/g cm^{-3}	1.608	1.660
μ/mm^{-1}	0.988	1.303
Independent reflections	2133	2942
Observed reflections ($I > 2\sigma(I)$)	1414	1897
Refined parameters	121	113
R1 (F^2)^a	0.096	0.0557
$wR2$ (F^2)^b	0.284	0.1462
S	1.450	1.035

^{a} R1= $\Sigma||F_o| - |F_c||/\Sigma|Fo|$. ^{b} $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2]/\Sigma w|F_o|^2]^{1/2}$.

Pascal's constants[31] as -174×10^{-6} (**1**), -243×10^{-6} (**2**), and -82×10^{-6} (**3**) cm³ mol^{-1}.

Crystallographic data collection

Suitable single crystals of **1** and **2** were mounted on an Enraf-Nonius MACH-3 four-circle diffractometer.[32,33] Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data of 25 reflections within $6° < \theta < 18°$. Data were collected at 293(2) K using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) and the ω-scan technique. A summary of the crystallographic data and structure refinement is given in Table 2. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS-97 and SHELXL-97 programs.[34,35] Notes on the refinement: in compound **1** a positional disorder was modeled for the 2,4′-bipyridine group, however the displacement of its group were not large enough to warrant its splitting, also not H-atoms of this group were positioned. In **2** all non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the malonate ligand and the water molecule were located from difference maps and refined with isotropic temperature factors and the hydrogen atoms of the 4,4′-bipyridine ligand were set in calculated positions and refined as riding atoms with a common isotropic thermal parameter for **2**. The final geometrical calculations and the graphical manipulations were carried out with the PARST95[36] and PLATON[37] programs, respectively.

CCDC reference numbers 185412 and 185413 for **1** and **2**, respectively.

See http://www.rsc.org/suppdata/dt/b3/b300291h/ for crystallographic data in CIF or other electronic format.

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