Structural and Magnetic Properties of Two Carboxylato-Bridged Manganese(II) Complexes with N-Donor Coligands

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Two polymeric Mn^{II} complexes, $[(m\text{-phth})(Mn)(bpp)_2]\cdot 0.5H_2O$ (**1**) and $[(mal)_2(Mn)_2(H_2O)_2(hmt)]$ (**2**) [mal = malonate; hmt = hexamethylenetetramine; bpp = 1,3-bis(4-pyridyl)propane; *m*-phth = 1,3-benzenedicarboxylate] have been synthesized. Complex **1** consists of 1D chains (with monocoordinated bpp) that are held together to form a 2D extended network of hydrogen bonding between lattice water molecules and uncoordinated bpp donors. Variable-temperature magnetic susceptibility data of the complex have been fitted applying the formula used for dinuclear complexes of Mn^{II} ions, considering interdimer interactions (J'). The following parameters were obtained from the best fit: $J = -0.88 \pm 0.02$ cm^{-1}, $J' = -0.1$ cm^{-1} and $g = 1.99 \pm 0.01$. The agreement factor $R = \Sigma(\chi_m T_{obsd.} - \chi_m T_{calcd.})^2/\Sigma(\chi_m T_{calcd.})^2$ is 1.1×10^{-5}. Complex **2** is a 3D polymeric network where *syn/anti*-bridging malonate ligands and Mn^{II} centers are assembled in the form of $[Mn(H_2O)(mal)]_n$ layers, which are further connected by hexamethylenetetramine. The magnetic data have been fitted considering the complex as a pseudo-two-dimensional sheet of Mn^{II} cations and malonate anions since the coupling through the hexamethylenetetramine ligand is almost zero. We have followed two approaches for fitting the data, (a) through the expansion series of Line's equation for the $S = 5/2$ antiferromagnetic quadratic layer and (b) by using the equation based on an infinite 2D square lattice composed of isotropically coupled classical spin $S = 5/2$. Both approaches result in excellent theoretical fits and similar J values of -0.24 cm^{-1} and -0.21 cm^{-1} for the Line's and Curély equations, respectively.

Introduction

Carboxylates are interesting ligands because of their wide variety of coordination modes which make them an attractive choice for the synthesis of polynuclear metal complexes, from discrete dimer to 1D, 2D, or 3D networks.[1] Metal-organic frameworks built up by transition metal cations and dicarboxylate anions are of interest from a variety of viewpoints, including magnetic materials,[2] open-framework structures with micropores for ion exchange or catalysis[3] and also compounds that are biologically relevant.[4] Therefore, a considerable number of transition metal compounds using dicarboxylates have been reported during the last decade.[1−8] In our own investigations we also prepared and characterized several coordination polymers of transition metals containing dicarboxylate groups in combination with multidentate N-donor coligands such as 4,4′-bipyridine, pyrazine, 1,2-bis(4-pyridyl)ethane etc.[5−8] In continuation of our interest in this research field, we have synthesized two new polynuclear Mn^{II}−dicarboxylate complexes. Complex **1**, $[(m\text{-phth})Mn(bpp)_2]\cdot 0.5H_2O$ [bpp = 1,3-bis(4-pyridyl)propane; *m*-phth = 1,3-benzenedicarboxylate], is a 1D chain comprising a rigid dicarboxylate and a flexible N-donor coligand, whereas complex **2**, $[(mal)_2(Mn)_2(H_2O)_2(hmt)]$ [mal = malonate; hmt = hexamethylenetetramine] is a 3D coordination polymer derived from a flexible dicarboxylate and a rigid N-donor coligand. Both complexes show weak antiferromagnetic interactions between the metal centers. Magnetic data have been fitted using different theoretical approaches.

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Results and Discussion

Synthesis of the Complexes

The complexes have been synthesized adopting procedures which are schematically given below:

$$MnCl_2 \cdot 4H_2O + 2\,bpp + Na_2(m\text{-phth}) \xrightarrow[\text{water/methanol (2:1)}]{\text{refluxing (1h)}} [(m\text{-phth})Mn(bpp)_2] \cdot 0.5H_2O\ (\mathbf{1}) + 2\,NaCl + 3.5\,H_2O$$

$$2\,MnCl \cdot 4H_2O + hmt + 2\,Na_2(mal) \xrightarrow[\text{water/methanol (2:1)}]{\text{stirring (1h)}} [(mal)_2Mn_2(H_2O)_2(hmt)](\mathbf{2}) + 4\,NaCl + 6\,H_2O$$

Description of the Structures

Complex 1

The structure of **1** consists of 1D polymeric chains (see Figures 1 and 2), built up by distorted octahedral Mn^{II} centers with dicarboxylate anions and *trans*-situated monocoordinated 1,3-bis(4-pyridyl)propane. One of the carboxylate groups of *m*-phthalate acts as a chelating ligand while the other, in a distorted *syn-syn* conformation, as bismonodentate) towards two crystallographically related metal centers, yielding a ribbon running parallel to the *b* axis. The polymer displays centro-symmetric 8- and 16-membered rings with metal−metal separations of 4.397 and 7.276 Å, respectively (Figure 1). The benzene ring forms a dihedral angle of 25.6(1)° with the former carboxylate but is almost coplanar with the other [angle of 8.7(1)°], resulting in a rather undulated chain. Thus the hexacoordinate Mn center possesses an N_2O_4 environment by virtue of four carboxylate oxygen atoms, and two bpp nitrogen donors. In the equatorial plane, the Mn−O(3) and Mn−O(4) distances of 2.113(2) and 2.114(2) Å, respectively, are in the range of those observed in Mn(*m*-phth) structures containing 2,2′-bipy[9] or 1,10-phen[10] ligands. On the other hand, the Mn−O distances generated by the chelating carboxylate are somewhat longer [2.262(2) and 2.288(2) Å] and appear comparable in length with the axial Mn−N bonds [Mn−N(1) = 2.313(3), Mn−N(2) = 2.285(3) Å, Table 1]. The two crystallographically independent flexible bpp ligands assume *gauche*/*anti* and *gauche*/*gauche* conformations, with the torsion angles along the propane chain being 64.3(5), 171.6(4)° and 71.7(11), 67.8(11)°, respectively. A disordered lattice water molecule connects the uncoordinated bpp nitrogen atoms of adjacent chains (N−O distances of ca. 3.0 Å) through hydrogen bonds, promoting the dimensionality of the compound. However, based on the

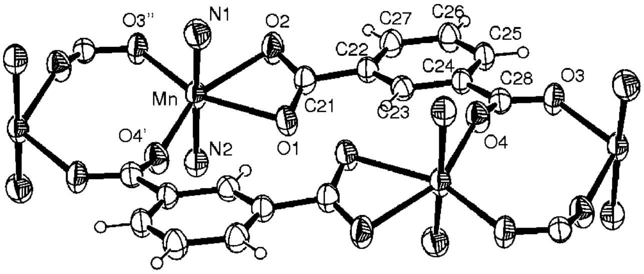

Figure 1. ID polymeric structure of **1** developed along axis *b*, showing the metal coordination environment (ellipsoid probability 40%); O4′ at: 1 − *x*, 1 − *y*, 1 − *z*; O3′′ at: *x*, 1 − *y*, *z*

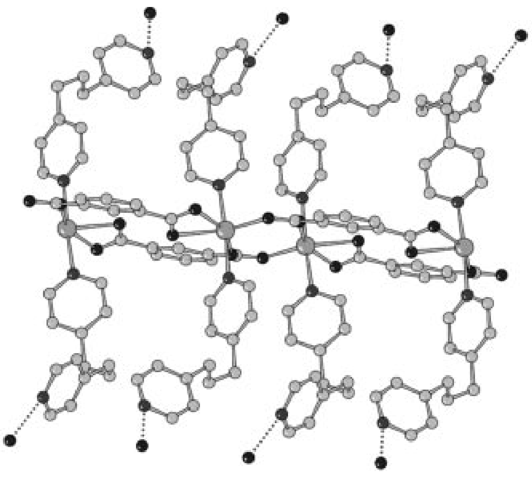

Figure 2. Polymeric chain of **1** showing bpp ligands hydrogen-bonded (dotted lines) to lattice water molecules through uncoordinated nitrogen atoms

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1** and **2**

Complex 1			
Distances [Å]			
Mn−O(3′′)	2.113(2)	Mn−O(2)	2.288(2)
Mn−O(4′)	2.114(2)	Mn−N(1)	2.313(3)
Mn−O(1)	2.262(2)	Mn−N(2)	2.262(2)
Angles [°]			
O(3′′)−Mn−O(4′)	112.58(8)	O(1)−Mn−N(1)	88.1(1)
O(3′′)−Mn−O(1)	151.56(8)	O(1)−Mn−N(2)	88.41(9)
O(3′′)−Mn−O(2)	94.17(8)	O(2)−Mn−N(1)	89.5(1)
O(3′′)−Mn−N(1)	97.4(1)	O(2)−Mn−N(2)	94.15(9)
O(3′′)−Mn−N(2)	88.76(9)	N(1)−Mn−N(2)	172.64(9)
O(4′)−Mn−O(1)	95.38(8)	C(21)−O(1)−Mn	90.36(16)
O(4′)−Mn−O(2)	153.22(8)	C(21)−O(2)−Mn	89.33(17)
O(4′)−Mn−N(1)	88.5(1)	C(28′′)−O(3′′)−Mn	125.40(19)
O(4′)−Mn−N(2)	85.41(9)	C(28′)−O(4′)−Mn	152.1(2)
O(1)−Mn−O(2)	57.85(7)		

Symmetry codes: ′: 1 − *x*, 1 − *y*, 1 − *z*; ′′: *x*, 1 − *y*, *z*

Complex 2			
Distances [Å]			
Mn−O(1)	2.154(2)	Mn−O(1w)	2.235(3)
Mn−O(2)	2.163(2)	Mn−N(1)	2.342(3)
Angles [°]			
O(1)−Mn−O(1′)	83.0(1)	O(2)−Mn−O(1w)	89.46(7)
O(1)−Mn−O(2)	86.43(8)	O(2)−Mn−N(1)	84.66(6)
O(1)−Mn−O(2′)	169.40(7)	O(1w)−Mn−N(1)	170.4(1)
O(1)−Mn−O(1w)	91.51(8)	C(1)−O(1)−Mn	129.8(1)
O(1)−Mn−N(1)	95.66(8)	C(1)−O(2′′)−Mn′′	130.8(2)
O(2)−Mn−O(2′)	104.1(1)		

Symmetry codes: ′: *x*, −*y*, *z*; ′′: 1/2 − *x*, 1/2 − *y*, 1/2 + *z*; ′′′: −*x*, −*y*, *z* peak height in the difference Fourier map, an occupancy factor of 0.5 was assigned to this water oxygen atom.

Complex 2

The X-ray structural determination of **2** evidences covalently bonded $[Mn(H_2O)(mal)]_n$ layers connected by hmt ligands to form a 3D polymer. The malonate anion, in its frequently found coordination mode[11−13] acts as a chelating and a bis(monodentate) ligand towards three metal ions. A selection of bond lengths and angles is reported in Table 1, and the structure with the atomic labeling scheme is shown in Figure 3. The octahedral coordination geometry of the metal atom consists of four planar equatorial carboxylate oxygen atoms [Mn−O(1) = 2.154(2) and Mn−O(2) = 2.163(2) Å], while the axial positions are occupied by an axial water molecule and an hmt nitrogen atom with significantly longer bond lengths [Mn−O(1w) = 2.235(3), Mn−N(1) 2.342(3) Å; Table 1]. These distances are similar to those found in the analogous $[Mn_2(mal)_2(4,4'\text{-bipy})(H_2O)_2]_n$,[11] with the exception of a slightly longer Mn−N(hmt) bond in the present case. In the square grids (4,4) of side dimension 5.517 Å, the coordinated water molecule forms two intralayer hydrogen bonds (2.719 Å) with the oxygen atoms of the anion chelating neighboring metal atoms (Figure 4). It is worth noting some features emerging from the 3D structure of the present compound and of the derivative containing the 4,4′-bipy ligands.[11] Figures 5, 6 and 7 show similar $[Mn(H_2O)(mal)]_n$ undulated layers with a zig-zag arrangement of the equatorial coordination planes. However, in the presently reported compound **2**, the sheets are separated by 8.029 Å and stack on top of each other with reference to a symmetry plane. The adamantoid hmt ligands connect the metal ions at 6.29 Å with angular Mn−N(hmt)−Mn links that outline a herringbone arrangement. A view of the packing along axis *c* indicates channels formed by the mal(Mn) layers and hmt ligands, the filled space being 74.8% (Figure 6). On the other hand, in $[Mn_2(mal)_2(4,4'\text{-bipy})(H_2O)_2]_n$, the distance between the mean planes through the sheets is slightly larger, 9.386 Å, but the rod-like 4,4′-bipy spacers cause sliding between the connected layers (Figure 7).

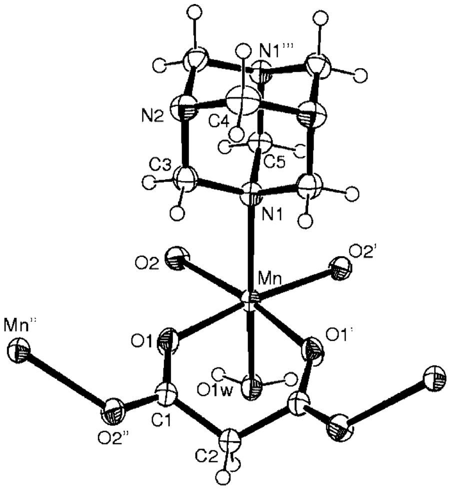

Figure 3. Structural fragment showing the Mn^{II} coordination sphere of **2** (ellipsoid probability at 40%); the hmt base is centered about an *mm2* crystallographic site (the twofold axis passing through C4−C5)

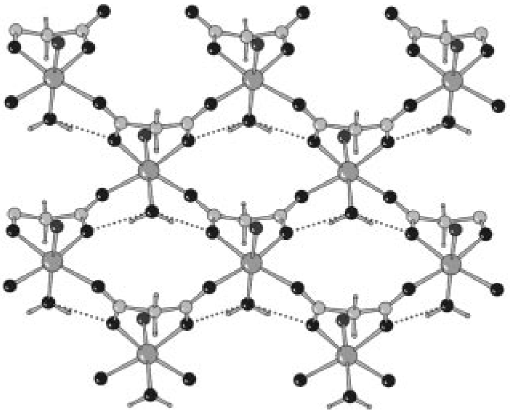

Figure 4. The $[Mn(H_2O)(malonate)]_n$ layer of complex **2** in the *bc* plane with hydrogen bonds (indicated by dotted lines) formed by the water molecules (for hmt only N donors are indicated)

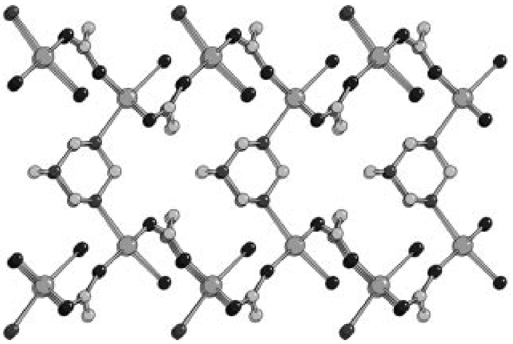

Figure 5. Crystal packing in **2** along axis *b* with staircase-like arrangement of $[Mn(H_2O)(mal)]_n$ layers

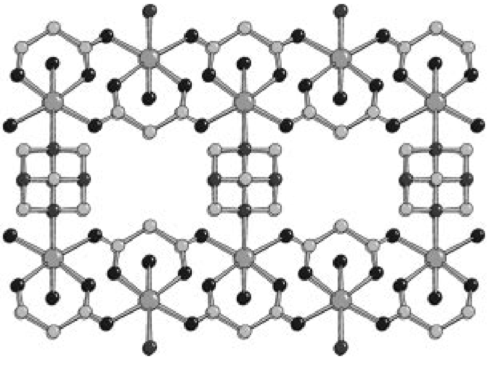

Figure 6. View of crystal packing in **2** along axis *c*, evidencing voids between hmt ligands

Magnetic Properties

Complex 1

The temperature dependence of χ_M (inset) and $\chi_M T$ (χ_M being the magnetic susceptibility for two Mn^{II} ions) for complex **1** is shown in Figure 8. The χ_M value (0.028

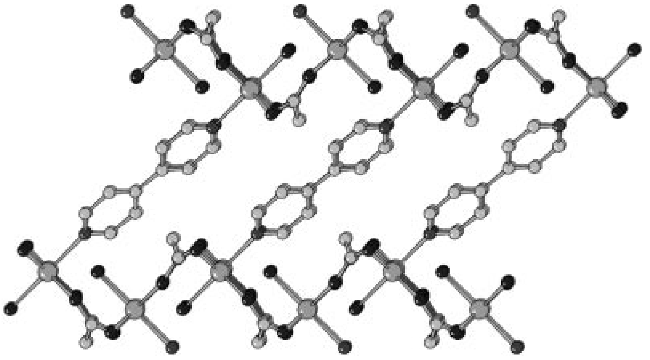

Figure 7. Crystal packing of $[Mn_2(mal)_2(4,4'\text{-bipy})(H_2O)_2]_n$ with layers connected by 4,4′-bipy ligands

cm^3mol^{-1} at 300 K) increases on decreasing the temperature. From room temp. to 100 K there is a smooth increase and from 100 K to 2 K the increase is more pronounced with a maximum at 4 K (χ_M = 0.717 cm^3mol^{-1}). Finally from 4 K to 2 K there is a slight decrease to 0.68 cm^3mol^{-1} at 2 K. χ_MT at 300 K is 8.42 $cm^3mol^{-1}K$, a value which is as expected for two "isolated" Mn^{II} ions. χ_MT is almost invariable up to 100 K and then gradually decreases while cooling to reach 1.36 $cm^3mol^{-1}K$ at 2 K. The shape of these curves is characteristic of the occurrence of weak antiferromagnetic interactions between the Mn^{II} centers.

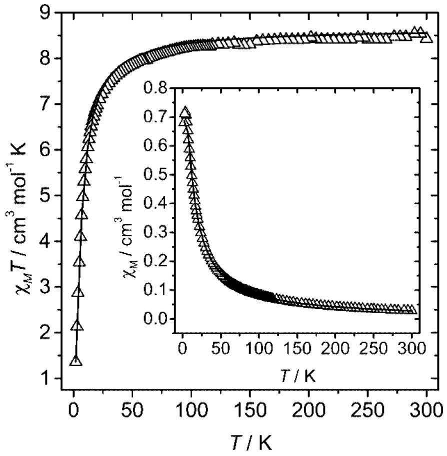

Figure 8. Temperature dependence (300−2 K) of χ_M (inset) and χ_MT (χ_M being the magnetic susceptibility for two Mn^{II} ions) for complex **1**; the solid line represents the best theoretical fit (see text for details)

The structure is one-dimensional, but from a magnetic point of view it can be considered as a dinuclear entity in which two Mn^{II} ions are linked by two distorted *syn-syn*-carboxylate bridges. These entities are linked together by an *m*-phthalate unit [monodentate to one Mn^{II} ion and chelated to the other], through a skeleton of five carbon atoms at distance of 7.276 Å. Thus, the only magnetic pathway is through Mn−O(4)−C(28)−O(3)−Mn in *syn-syn* conformation, which creates weak antiferromagnetic coupling (see below),[1b,14] although weak ferromagnetic coupling has also been reported in some cases.[2e]

Taking into account the pseudo-dinuclearity of **1**, the susceptibility data have been fitted applying the formula for a dinuclear complex of Mn^{II} (S = 5/2),[14] and the initial results were improved by adding a possible J' (intermolecular coupling) using the mean-field approach. The employed Hamiltonian was $H = -JS_1S_2 + g\beta S_zH - zJ'\langle S_z\rangle S_z$.[1b] The best fit is given by the following parameters: $J = -0.88 \pm 0.02$ cm^{-1}, $J' = -0.1$ cm^{-1} and $g = 1.99 \pm 0.01$. The factor $R = \Sigma(\chi_mT_{obsd.} - \chi_mT_{calcd.})^2/\Sigma(\chi_mT_{calcd.})^2$ is 1.1×10^{-5} corroborating an excellent agreement between experiment and theory.

Complex 2

The temperature dependence of χ_M (inset) and χ_MT (χ_M being the magnetic susceptibility for one Mn^{II} ion) for complex **2** is shown in Figure 9. The χ_M value is 0.0144 cm^3mol^{-1} at 295 K. On decreasing the temperature the value of χ_M increases; from room temperature to 100 K there is a smooth increase and from 100 K to 2 K the increase is more pronounced (χ_M = 0.54 cm^3mol^{-1} at 2 K). In this case there is no maximum in the χ_M curve, as observed in complex **1**; only a tendency to a maximum is shown close to 2 K. χ_MT at 300 K is 4.24 $cm^3mol^{-1}K$, a value which is as expected for an "isolated" Mn^{II} ion. χ_MT is almost invariable up to 100 K (4.10 $cm^3mol^{-1}K$) and gradually decreases while cooling to reach 1.08 $cm^3mol^{-1}K$ at 2 K. The shape of these curves is characteristic of the occurrence of weak antiferromagnetic interactions between the Mn^{II} centers.

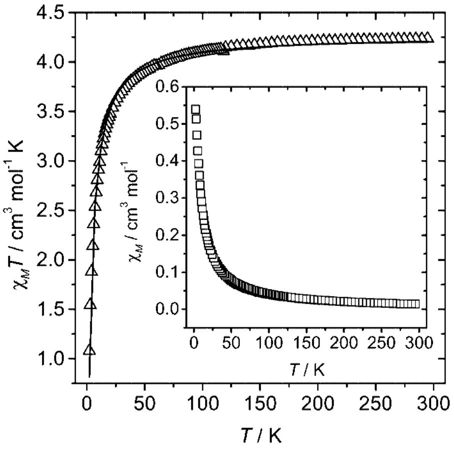

Figure 9. Temperature dependence (300−2 K) of χ_M (inset) and χ_MT (χ_M being the magnetic susceptibility for one Mn^{II} ion) for complex **2**; solid line represents their best theoretical fit (see text for details)

Taking into account that the structure is a three-dimensional network, it is impossible to fit the susceptibility data in order to find an appropriate J value. But, the structure can be considered as two-dimensional sub-lattices, consisting of Mn^{II} ions and malonate bridging ligands (Figure 4), which are linked to each other by hmt ligands. The Mn−N(1) distance [2.342(3) Å] is the longest in the distorted octahedral environment of Mn^{II}, which serves to simplify the calculations. The Mn−O(1) and Mn−O(2) distances [malonate bridge Mn−O(2)−C(1)−O(1)−Mn in *syn-anti* conformation] are shorter [2.154(2) and 2.163(2) Å, respectively]. Thus, owing to these differences in Mn−O/N distances and the large Mn−Mn separation (8.029Å), we can assume that the magnetic coupling through hmt will be almost negligible. Thus, with the pseudo two-dimensional character of **2**, the susceptibility data have been fitted according to two approaches:

a) By the expansion series[15] of Line's equation for an $S = 5/2$ antiferromagnetic quadratic layer, based on the exchange Hamiltonian $H = -\Sigma_{nn}\mathrm{J}\mathrm{S_i}\mathrm{S_j}$, where Σ_{nn} runs over all pairs of nearest-neighbor spins i and j [Equation (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.

$$Ng^2\beta^2/\chi|J| = 3\theta + (\Sigma C_n/\theta^{n-1}) \qquad (1)$$

The best fit is obtained with $J = -0.24 \pm 0.03\ \mathrm{cm^{-1}}$ and $g = 1.99 \pm 0.01$. The factor $R = \Sigma(\chi_\mathrm{m}T_\mathrm{obsd.} - \chi_\mathrm{m}T_\mathrm{calcd.})^2/\Sigma(\chi_\mathrm{m}T_\mathrm{calcd.})^2$ is 1.57×10^{-4}, which actually corresponds to an excellent experiment-theory agreement.

b) By means of the analytical expression derived by Curély for an infinite 2D square lattice composed of classical spins ($S = 5/2$), isotropically coupled, and based on the exchange Hamiltonian $H = -\Sigma_{nn}JS_iS_j$, where S_{nn} runs over all pairs of nearest-neighbor spins i and j (Heisenberg couplings)[16] [Equation (2)], where N is the Avogadro number, β the Bohr magneton, k the Boltzmann constant, and u is the well-known Langevin function defined as $u = L[JS(S+1)/kT] = \coth[JS(S+1)/kT] - kT/JS(S+1)$.

$$\chi = [Ng^2\beta^2S(S+1)(1+u)^2]/[3kT(1-u)^2] \qquad (2)$$

The best fit leads to $J = -0.21 \pm 0.01\ \mathrm{cm^{-1}}$; $g = 1.99 \pm 0.01$. The factor $R = \Sigma(\chi_\mathrm{m}T_\mathrm{obsd.} - \chi_\mathrm{m}T_\mathrm{calcd.})^2/\Sigma(\chi_\mathrm{m}T_\mathrm{calcd.})^2$ is 1.46×10^{-4}, which gives excellent agreement between experimental and theory.

The J values obtained by Line's or Curély expressions are very close: $-0.24\ \mathrm{cm^{-1}}$ and $-0.21\ \mathrm{cm^{-1}}$, respectively. Taking into account that the Curély formula is more accurate and is valid up to 0 K (the Line's formula is only valid up to the maximum of χ_M, approximately), the value of $-0.21\ \mathrm{cm^{-1}}$ seems to be the most precise for **2**.

Conclusion

As indicated in recent papers on manganese carboxylate, the most common feature for carboxylate bridges is the *syn-syn* mode.[17] The *syn-anti* bridge appears to be rather uncommon for $\mathrm{Mn^{II}}$ complexes, and only in a few cases have the magnetic properties been reported to date.[11,17,18] Corbella et al. have recently demonstrated that magnetic interactions through a *syn-anti*-carboxylate bridge in manganese complexes should be very sensitive to small structural changes: Mn−O distances, the O_{anti}−Mn−O_{syn} angle, the planarity of the bridge, etc.[19] A complete Table of this kind of complexes, including the magnetic data, has recently been gathered by Durot et al.[17] In general, *syn-anti* bridges induce very small antiferromagnetic J values because of the mismatch in the orientation of magnetic orbitals. All reported exchange coupling constants are reported to be between 0 cm^{-1} (no coupling) and −2 cm^{-1}.

Thus, although both complexes **1** and **2** have the same kind of bridging ligand; carboxylate in a distorted *syn-syn* conformation for **1** and a *syn-anti* conformation for **2**, the more antiferromagnetic J value in **1** can be ascribed to the smaller Mn−O distances (2.113 and 2.114 Å) in comparison with those found in **2** (2.154 and 2.164 Å). Moreover, in complex **2**, the simultaneous presence of hmt, as the bridging ligand that is further away, allows us to attribute the weak antiferromagnetic coupling only to the carboxylate bridging group. A contribution from the hmt ligand (if any) should be partial and very small.

Experimental Section

Materials: High-purity 1,3-bis(4-pyridyl)propane (bpp) and hexamethylenetetramine (hmt, also known as urotropine) were purchased from Aldrich Chemical Company Inc. and E. Merck (India) Ltd., respectively, and used as received. All the other chemicals were of A.R. grade.

Physical Measurements: Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin−Elmer elemental analyzer. IR spectra (4000−600 cm^{-1}) were taken in KBr pellets using a Jasco FT-IR (model 300E). The magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS SQUID magnetometer (applied field 0.1 T) working in the temperature range 300−2 K. Diamagnetic corrections were estimated from Pascal's tables.[1b]

X-ray Structure Determination: Diffraction data of both structures were collected at room temperature with a Nonius DIP-1030H system equipped with a graphite monochromator and Mo-K_α radiation ($\lambda = 0.71073$ Å). A total of 30 frames were collected, each with an exposure time of 20 min with a rotation angle of 6° about φ, the detector being at 90 mm from the crystal. Cell refinement, indexing and scaling for both the data sets were carried out using Mosflm[20] and Scala.[20] The structures were solved by Patterson and Fourier analyses[21] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[21] Hydrogen atoms were located in idealized geometries. All the calculations were performed by means of the WinGX System, Ver. 1.64.05.[22] The crystal data and structure refinements are given in Table 2. CCDC-231735 (**1**) and -231736 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of [(*m*-phth)Mn(bpp)$_2$]·0.5H$_2$O (1): An aqueous solution (5 mL) of bpp = 1,3-bis(4-pyridyl)propane (2 mmol, 0.369 g) was added dropwise to an aqueous solution (5 mL) of $\mathrm{MnCl_2{\cdot}4H_2O}$ (1 mmol, 0.197 g) with constant stirring for 5 min until the mixture became turbid. To this resulting mixture an aqueous solution (5 mL) of disodium *m*-phthalate (1 mmol, 0.210 g) was added dropwise yielding a transparent solution. The reaction mixture was refluxed for 1 h and filtered, the filtrate was kept in a $\mathrm{CaCl_2}$ desiccator. After a few days, colorless crystals suitable for X-ray analysis

Table 2. Crystal data and refinement details of complexes **1** and **2**

	1	**2**
Empirical formula	$C_{34}H_{33}MnN_4O_{4.50}$	$C_{12}H_{20}Mn_2N_4O_{10}$
Formula mass	624.58	490.20
T [K]	293(2)	293(2)
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Imm*2
a [Å]	9.444(2)	16.058(3)
b [Å]	10.226(3)	7.704(2)
c [Å]	16.511(3)	7.098(3)
α [°]	85.09(2)	90.00
β [°]	77.16(1)	90.00
γ [°]	80.08(1)	90.00
V [Å^3]	1529.6(6)	878.1(5)
Z	2	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.356	1.854
μ(Mo-K_α) [mm^{-1}]	0.478	1.502
F(000)	652	500
Reflections collected	10176	1522
Unique reflections/R(int)	6145 /0.0449	1443 /0.0433
Reflections observed [$I > 2\sigma(I)$]	4332	1400
No. parameters refined	403	79
$R1$	0.0514	0.0349
$wR2$	0.1338	0.0880
GoF	1.040	1.121
Residuals [e·Å^{-3}]	0.458, −0.456	0.466, −0.325

were obtained. Yield 0.437 g (70%). $C_{34}H_{33}MnN_4O_{4.5}$ (624.58): calcd. C 65.38, H 5.29, N 8.97; found C 65.65, H 5.22, N 8.91. IR: $\tilde{\nu}$ = 3429 (w, v br.), 3071 (w), 2925 (w), 1610 (vs), 1570 (s), 1543 (s), 1447 (m), 1390 (vs), 1222 (w), 1023 (w), 752 (m) 716 (w), 512 (vw) cm^{-1}.

Synthesis of [(mal)$_2$(Mn)$_2$(H$_2$O)$_2$(hmt)] (2): An aqueous solution (5 mL) of hmt (0.5 mmol, 0.070 g) was added dropwise, with constant stirring, to a methanolic solution (5 mL) of $MnCl_2{\cdot}4H_2O$ (1 mmol, 0.197 g). An aqueous solution (5 mL) of disodium malonate (1 mmol, 0.148 g) was added to this solution yielding a colorless compound. The single crystals suitable for X-ray analysis were obtained by allowing a methanolic solution (10 mL) of $MnCl_2{\cdot}4H_2O$ to diffuse into an aqueous layer of disodium malonate and hmt (1:1 mixture) (10 mL) in a tube. The colorless crystals were found at the junction of the two solutions after three weeks. Yield 0.147 g (60%). $C_{12}H_{20}Mn_2N_4O_{10}$ (490.20): calcd. C 29.38, H 4.08, N 11.42; found C 29.65, H 3.97, N 11.61. IR: $\tilde{\nu}$ = 3436−3239 (s, v br.), 2980 (w), 1572 (vs), 1445 (m), 1357 (s), 1225 (m), 1025 (w), 992 (s), 691 (m), 577 (w) cm^{-1}.

Supporting Information: A figure showing the 2D sheet of complex **1** (formed by hydrogen bonding between the lattice water and uncoordinated bpp nitrogen atoms of the adjacent chains) and a table containing the H bond parameters [Å, °] for **1** and **2** have also been deposited.

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