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Article

Structural and Magnetic Properties of Carboxylato-Bridged Manganese(II) Complexes Involving Tetradentate Ligands: Discrete Complex and 1D Polymers. Dependence of *J* on the Nature of the Carboxylato Bridge

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The crystal structure of an inorganic linear polymer consisting of Mn(II) and an N-centered tripodal ligand *N,N*-bis(2-(6-methyl)pyridylmethyl)glycinate is presented (**1**, $C_{16}H_{20}N_3O_3F_6P_1Mn_1$, $a = 9.993(2)$ Å, $b = 13.285(3)$ Å, $c = 16.040(3)$ Å, orthorhombic, *Pnam*, $Z = 4$). The polymeric structure is ensured by carboxylato ligands connecting two Mn(II) in a rather rare syn-anti geometry. The magnetic properties of this infinite chain have been investigated, together with the magnetic properties of a dimeric Mn(II) compound (**3**) from a closely related ligand [*N,N*-bis[(1-methylimidazol-2-yl)-methyl)glycinate] involving an unusual bis(monatomic-carboxylato) bridge. The inorganic polymer **1** shows a pseudo-2D magnetic structure, with a major interaction pathway along the chain ($J/k = -0.172 \pm 0.005$ K) and an interchain minor one ($zJ'/k = -0.006 \pm 0.004$ K). These properties are reminiscent of those from a closely related previously reported inorganic Mn(II) polymer (**2** obtained from manganese(II) and *N,N*-(2-pyridylmethyl)-((1-methylimidazol-2-yl)methyl)glycinate). The dimer **3** shows a small antiferromagnetic coupling of $J/k = -0.693 \pm 0.016$ K. To address the influence of the carboxylato bridging mode on the magnetic properties, these complexes are compared to a series of compounds involving carboxylato bridges of several geometries between Mn(II) ions. Carboxylato bridges induce usually antiferromagnetic coupling, with the magnitude of the interaction ($|J|$) increasing with the number of bridges. The *J* value is dependent on the bridging mode. The syn-syn bridge is an efficient pathway, even by comparison with the monatomic [$(\mu\text{-}\eta^1\text{-carboxylato})$] bridge.

Introduction

Carboxylates are interesting ligands both because they can assume a large palette of coordination modes (from terminal monodentate to bridging in several configurations, see examples in Figure 1) and because of their biological relevance.[1–4] The carboxylato moiety provided either by glutamate or by aspartate is one of the most frequent ligands for transition metals encountered in metalloproteins. They are recognized to play a key role in modulating activity of metal centers in metalloproteins through fine-tuning of thermodynamic properties achieved by shifts from one coordination mode to another and acid−base equilibria.[2,3,5,6] Their wide variety of coordination modes make them also

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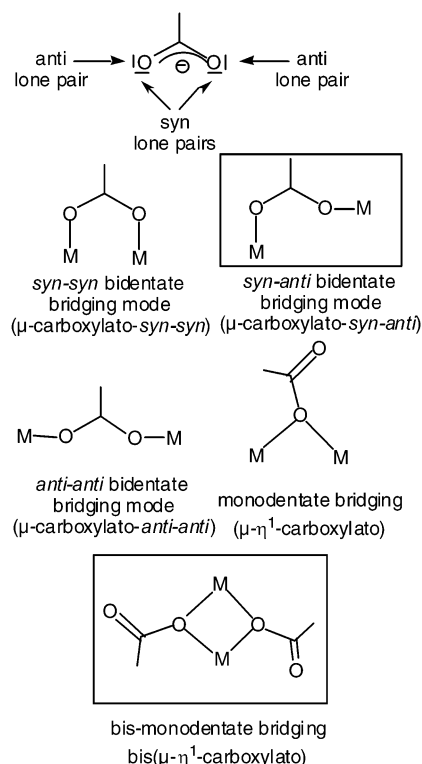
Figure 1. Carboxylate: syn and anti lone pairs and bridging modes. Bridges involved in compounds **1**, **2**, and **3** are framed.

key building blocks for the synthesis of polynuclear complexes, from discrete dimer to supramolecular 1D, 2D, or 3D networks.[7−13] Current literature reveals that efforts are being made to better understand the control of nuclearity and dimensionality and the control of the bridging mode in such entities.[12,14−16]

We have initiated the synthesis of a series of biomimetic ligands bearing both a carboxylate and N-heterocycles of different bulkiness in order to prepare Mn(II) complexes.[17,18] Whereas iron(III) and iron(II) led to mononuclear complexes,[19] manganese(II) was shown to produce a richer variety of structures in the solid state.[17,18] Compound **1**, involving manganese(II) and *N,N*-bis(2-(6-methyl)pyridyl-methyl)glycinate BMPG [acronym for (bis-methylpyridine)-

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glycinate], crystallizes from water in a polymeric chain. We report here its structure, which is reminiscent of the structure of compound **2** obtained from manganese(II) and *N,N*-(2-pyridylmethyl)((1-methylimidazol-2-yl)methyl)glycinate IPG [acronym from imidazole pyridine glycinate].[17] With a closely related ligand, namely, *N,N*-bis[(1-methylimidazol-2-yl)methyl]glycinate BIG [acronym for bis imidazole glycinate], a dinuclear μ-η^1-carboxylato−Mn(II)Mn(II) complex **3** was obtained, and its structure has been previously described.[18] The conformations of the bridging carboxylates found in these compounds are rather rare:[2] either mono-carboxylato syn-anti in the two polymeric forms **1** and **2**, or bis-monatomic bridging in the dimer **3**. We report here the magnetic properties of **1** and **3**, and we discuss them in comparison with **2** and other Mn(II)−μ-carboxylato compounds.

Experimental Section

IR spectra (KBr) were recorded on a Brüker IFS 66 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Brüker AC 250 spectrometer. Electronic absorption spectra were recorded on a Safas 190 DES double-mode spectrophotometer. Chemical reagents were purchased from either Aldrich or Acros and used without further purification.

***N,N,N*-[(Ethoxycarbonyl)methyl]bis(6-methyl-2-pyridylmethyl)-amine (First Method).** Ethyl iodoacetate (3.5 g, 16.4 mmol) was added to a deoxygenated solution of *N,N*-bis(6-methyl-2-pyridyl-methyl)amine[20] (3.433 g, 15.1 mmol) in anhydrous dimethylfor-mamide (160 mL) under argon atmosphere. Cesium carbonate (4.92 g, 15.1 mmol) was added at 0 °C. The resulting suspension was stirred at 45 °C for 15 h. After evaporation to dryness, CH_2Cl_2 was added and the resulting solution was filtered. The product was purified by chromatography, providing a yellow oil (SiO_2, CH_2-Cl_2/MeOH (100/0 to 90/10)). Yield: 3.934 g (83%). ^{1}H NMR (CDCl$_3$): δ = 1.21 (t, J = 7.33 Hz, 3H, C*H$_3$*CH$_2$COO), 2.46 (s, 6H, C*H$_3$*-py), 3.37 (s, 2H, N−C*H$_2$*COOEt), 3.90 (s, 4H, N−C*H$_2$*-py), 4.09 (q, J = 7.33 Hz, 2H, CH$_3$C*H$_2$*COO), 6.95 (d, J = 7.82 Hz, 2H, H$_{py}$), 7.34 (d, J = 7.82 Hz, 2H, H$_{py}$), 7.50 (t, J = 7.82 Hz, 2H, H$_{py}$). ^{13}C NMR (CDCl$_3$): δ = 14.1 (*C*H$_3$CH$_2$COO), 24.3 (*C*H$_3$-py), 52.7 (N−*C*H$_2$COOEt), 60.0 (N−*C*H$_2$−py), 60.3 (CH$_3$*C*H$_2$-COO), 119.6 (*C*H$_{py}$), 121.4 (*C*H$_{py}$), 136.6 (*C*H$_{py}$), 157.4 (*C*$_{py}$−CH$_3$), 158.4 (*C*$_{py}$−CH$_2$N), 171.2 (*C*O$_2$Et). MS (ES): m/z 314.2 [M + 1, 100%], 336.2 [M + Na, 100%].

***N,N,N*-[(Ethoxycarbonyl)methyl]bis(6-methyl-2-pyridylmethyl)-amine (Second Method).** Under argon atmosphere, sodium cy-anoborohydride (0.229 g, 3.6 mmol) was added to a deoxygenated solution of 6-methyl-2-pyridinecarboxaldehyde (0.398 g, 3.3 mmol) and glycine ethyl ester hydrochloride (ClNH$_3$CH$_2$COOEt) (0.464 g, 3.3 mmol) in anhydrous MeOH (10 mL) at 0 °C. After 2 h at 0 °C, the mixture was stirred for 2 h at room temperature. The solution was then cooled to 0 °C, another equivalent of 6-methyl-2-pyridinecarboxaldehyde (0.403 g, 3.3 mmol) (in anhydrous MeOH, 5 mL) was added, and the reaction mixture was acidified by CF$_3$-COOH to pH 5.5. Then, sodium cyanoborohydride (0.229 g, 3.6 mmol) was added. After 2 h at 0 °C, the solution was stirred for 12 h at room temperature. Methanol was then evaporated, and the residual oil was extracted by CH_2Cl_2 from the aqueous phase (pH 7). The organic phases were dried over Na$_2$SO$_4$ and evaporated. The crude product was purified by column chromatography,

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providing a yellow oil (SiO₂, CH₂Cl₂/MeOH (100/0 to 90/10)). Yield: 0.782 g (76%). ¹H NMR, ¹³C NMR, and MS (ES) as described above.

Sodium N,N-Bis[2-(6-methyl)pyridylmethyl]glycinate (BMPG). BMPGNa was obtained by saponification at room temperature of N,N,N-[(ethoxycarbonyl)methyl]bis(6-methyl-2-pyridylmethyl)-amine (0.806 g, 2.58 mmol) in a 3 M solution of NaOH for 20 h (5 mL). The volume was then extended to 100 mL with bidistilled water, and the pH was adjusted to the 8−8.5 range (HCl, 6 M). After evaporation and drying under reduced pressure overnight over P₂O₅, residual NaCl was partially removed by extracting the carboxylate BMPGNa with anhydrous methanol. Yield: 0.756 g (91%). ¹H NMR (CDCl₃): δ = 2.29 (s, 6H, CH_3−py), 3.30, (s, 4H, N−CH_2py), 3.44 (s, 2H, N−CH_2COONa), 6.83 (m, 4H, H$_{py}$), 7.33 (m, 2H, H$_{py}$). ¹³C NMR (CDCl₃): δ = 23.7 (CH_3−py), 58.3 (N−CH_2COONa), 59.8 (N−CH_2−py), 119.6 (CH_{py}), 122.1 (CH_{py}), 137.2 (CH_{py}), 157.4 (C_{py}−CH₃), 157.7 (C_{py}−CH₂N), 174.7 (CO_2-Na). MS (ES): m/z 308.1 [M + 1, 100%].

[Mn(BMPG)(H₂O)], (PF₆) (1). Typically, polymeric chain crystals were obtained as followed. MnBr₂ (0.52 mmol, 112 mg) in deoxygenated bidistilled water (15 mL) was added to a solution of the ligand (180 mg, 0.58 mmol) in deoxygenated bidistilled water (10 mL). It was allowed to stand for 1 h 30 at 40 °C. Then, after cooling to room temperature, a deoxygenated solution of NH₄PF₆ (3 equiv, 260 mg) in bidistilled water (10 mL) was added dropwise. The solution was allowed to stand still for 3 weeks, and crystals were slowly grown (see crystal data below). For further characterizations, these crystals were ground and dried for 48 h under vacuum with P₂O₅. Yield: 120 mg (46%). Calcd for [C₁₆H₁₈N₃O₂-Mn(H₂O)]⁺, PF₆⁻: H, 4.01; C, 38.24; N, 8.37; P, 6.17; Mn, 10.94. Found: H, 4.07; C, 38.31; N, 8.31; P, 6.44; Mn, 10.31. IR (KBr cm⁻¹): 3562 ($\nu_{linked\ water}$),[18] 1608 (sh) and 1567 (ν_{asCO}), 1462 (ν_{sCO}), 853 (PF₆), 792 ($\nu_{py.\ deform.}$), 558 (PF₆) (strong bands only). MS (ES): m/z 697.2 (100%) [(MnBMPG)₂,H₂O + 1], 380.1 (28%) [MnBMPG-(H₂O) + Na].

Crystal Data, Data Collection, and Refinement. Crystals of [Mn(BMPG)OH₂] PF₆ (**1**) were obtained from aqueous solution as pale yellow prismatic crystals. One of these, of size 0.3 × 0.4 × 0.4 mm, was mounted on a SMART 1000 Bruker AXS diffractometer with Mo Kα radiation [λ = 0.7107 Å]. Of 1960 unique reflections measured, 945 with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by direct methods[21] and refined[22] on F^2 by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were calculated in ideal geometrical positions. Final refinement gave an R1 = 0.0647, wR2 = 0.1797. Experimental details for the X-ray data collection are reported in Table 1. Atomic scattering factors were taken from ref 23. The refinement procedure was carried out using the Wingx package[24] with the program PARST[25] for the geometrical description of the structures and ORTEP[26] and PLUTO[27] for the structure drawings.

Magnetic Measurements and Fitting. Magnetization data were collected on ground crystals by using a Quantum Design MPMS5.

Table 1. Crystallographic Data for **1**

empirical formula	C₁₆H₂₀N₃O₃P₁F₆Mn₁
molecular mass	502.254
crystal system	orthorhombic
space group	*Pnam*
a [Å]	9.993(2)
b [Å]	13.285(3)
c [Å]	16.040(3)
V [Å³]	2129.4(8)
Z	4
F(000)	1020
D_{calc} [Mg m⁻³]	1.566
μ(Mo Kα) [mm⁻¹]	0.77
crystal size [mm]	0.4 × 0.5 × 0.5
habit	prism
T [K]	293
no. of reflns measd	23091
θ range [deg]	2.00 < 2θ < 50.20
hkl ranges	−11 ≤ h ≤ 11, −15 ≤ k ≤ 15, −19 ≤ l ≤ 19
no. of unique reflns	1960
no. of reflns obsd $I > 2\sigma(I)$	945
no. of params	155
R1 [$I > 2\sigma(I)$]^a	0.0647
weight	1/$\sigma^2(F_o^2)$ + (0.0857P)² + 0.00P]^b
wR2^c	0.1797
max. Fourier diff [e/Å³]	0.76, −0.43

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} P = (Max(F_o^2,0) + 2F_c^2)/3. ^{c} wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$.

They were collected in the temperature region 2−300 K and within an applied field of 10 kG and 0.01 kG. The data were corrected for the diamagnetism contributions of the sample and of the cell. The experimental data were fitted to expressions derived according to the structure (dimer or infinite chain, see text) through two different and independent procedures derived from two different minimization algorithms (Marquardt algorithm (KaleidaGraph) and Nelder−Mead (or simplex downhill) algorithm).[28] They provided consistent results.

Dimer 3. The first procedure involved a sequential determination of parameters by a least squares minimization (with a Marquardt algorithm) as following: (i) g was obtained by fitting $1/\chi = f(T)$ in the high-temperature range (150−300 K). (ii) J was obtained by fitting the $\chi T = f(T)$ in the whole temperature range, keeping g fixed to the previously determined value. (iii) The simulation of $\chi T = f(T)$ was then improved by adding the contribution of a monomeric Mn(II) impurity (ρ) that could have arisen from bridge disrupture, keeping g and J fixed. At each step, the algorithm provided an uncertainty for the fitted parameter (g = 2.015 ± 0.001, J/k = −0.688 ± 0.011 K, ρ = (1.5 ± 0.4)%). In the second procedure, a Nelder−Mead algorithm was used. The same results were obtained whether all three parameters were allowed to vary simultaneously or with sequential determination of g, J, and ρ: g = 2.025, J/k = −0.697 K, ρ = 1%, R = 2.7 × 10⁻⁴.[29] The parameters are reported as average of the central value from the Marquardt algorithm and of the value from the Nelder−Mead algorithm. Uncertainties are given so as to account for the whole interval from the Marquardt algorithm: g = 2.020 ± 0.006, J/k = −0.693 ± 0.016 K, ρ = (1.5 ± 0.5)%. The experimental and calculated data are shown both as $\chi T = f(T)$ and $\chi = f(T)$ (see Figure 6) in the whole temperature range. It should be noted that uncertainties for parameters such as J are seldom provided in the literature.

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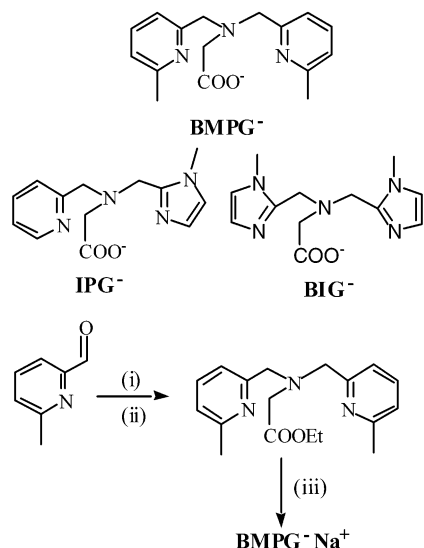
Figure 2. Ligands BMPG, IPG, and BIG and synthetic pathways to ligand BMPG. First method: (i) (a) NH_2OH, HCl H_2O/MeOH, H_2 20 bar, Pd/C; (b) 6-methyl-2-pyridinecarboxaldehyde, $NaBH_4$, anhydrous MeOH, 0 °C; (ii) ICH_2CO_2Et, Cs_2CO_3, DMF, 40 °C; (iii) 3 M NaOH, room temperature, 18 h. Second method: (i) $EtOOCCH_2NH_3Cl$, $NaBH_3CN$, anhydrous MeOH, 0 °C; (ii) 6-methyl-2-pyridinecarboxaldehyde, $NaBH_3CN$, anhydrous MeOH, 0 °C; (iii) 3 M NaOH, room temperature, 18 h.

Chain 1. Sequential determination of the three parameters (g, J, and J') was done, using either a Marquardt algorithm or a Nelder–Mead algorithm. (i) g was obtained by fitting $1/\chi = f(T)$ in the high temperature range (150–300 K). (ii) J was obtained by fitting the $\chi T = f(T)$ in the whole temperature range, keeping g fixed to the previously determined value. (iii) The simulation of $\chi T = f(T)$ was improved by adding the contribution of an interchain interaction, keeping g and J at fixed values. The Marquardt algorithm provided uncertainties for each parameter: ($g = 1.9642 \pm 0.0008$, $J/k = -0.1685 \pm 0.0013$ K, $zJ'/k = -0.004 \pm 0.002$ K). The Nelder–Mead algorithm provided the following parameters: $g = 1.965$, $J/k = -0.175$ K, $zJ'/k = -0.0075$ K, $R = 6.2 \times 10^{-5}$).[29] The parameters and uncertainties are reported so as to account for both the procedures, as for compound **1**: $g = 1.965 \pm 0.002$, $J/k = -0.172 \pm 0.005$ K, $zJ'/k = -0.006 \pm 0.004$ K. The experimental and calculated data are shown both as $\chi T = f(T)$ and as $\chi = f(T)$ (see Figure 7) in the whole temperature range.

Results and Discussion

Synthesis. Ligand Synthesis. A given N-centered tripod can be synthesized by several methods, depending on the order chosen for the introduction of the different moieties. As for the previously described ligand *N,N*-bis[(1-methylimidazol-2-yl)methyl]glycinate,[18,19] two synthetic routes to ligand *N,N*-bis[2-(6-methyl)pyridylmethyl]glycinate BMPG have been investigated (see Figure 2). The first strategy involved the preparation of *N,N*-bis(6-methyl-2-pyridylmethyl)amine from 6-methyl-2-pyridinecarboxaldehyde, according to the procedures found in the literature[20,30] (yield = 48%). The resulting amine was subsequently alkylated by ethyliodoacetate with cesium carbonate (yield = 83%). The overall yield for the preparation of the ester *N,N,N*-[(ethoxycarbonyl)methyl]bis(6-methyl-2-pyridyl-methyl)amine by this procedure is 40%. The second method

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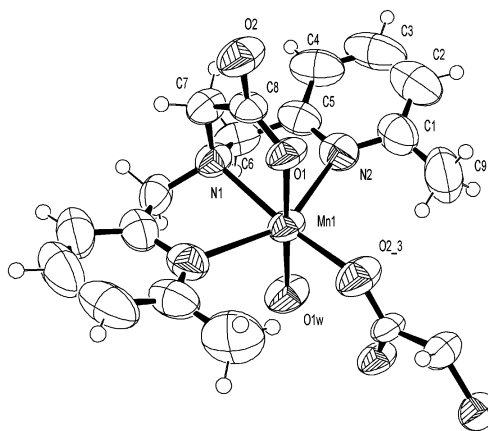
Figure 3. ORTEP drawing (50% probability ellipsoids) of the cationic moiety of compound **1**.

Table 2. Selected Distances (Å) and Angles (deg) for **1**

Mn1–O1	2.147(5)	O1–Mn1–O1W	179.3(2)
Mn1–O1W	2.178(5)	O1–Mn1–N1	78.9(2)
Mn1–N1	2.248(6)	O1–Mn1–N2	85.4(1)
Mn1–N2	2.363(5)	O1W–Mn1–N1	101.7(2)
Mn1–O2^a	2.071(5)	O1W–Mn1–N2	94.7(1)
		N1–Mn1–N2	74.2(1)

^{a} $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + \frac{1}{2}$.

consisted of a one-step reductive amination with sodium cyanoborohydride producing the ethyl ester from 6-methyl-2-pyridinecarboxaldehyde and glycine ethyl ester with an improved yield of 76%. Reductive amination has proven here again to be the more efficient route, as previously reported.[17] Ligand BMPG was then readily obtained after hydrolysis by a 3 M NaOH solution (yield = 91%).

Complex Preparation. Crystals of **1** suitable for single-crystal diffraction studies were grown in water by slow evaporation.

Description of the Structure of 1. Compound **1** crystallizes in the orthorhombic space group *Pnam*, and the asymmetric unit consists of a cationic manganese complex and, as a counterion, a hexafluorophosphate both lying on a symmetry plane. Experimental details for the X-ray data collection are reported in Table 1. Each Mn(II) ion is octahedrally surrounded by a BMPG ligand, a water molecule, and, occupying the remaining sixth position, a carboxylate oxygen of an adjacent molecule in position $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$ (Figure 3). The coordination polyhedron can be best described as a distorted octahedron as apparent from the bond distances and angles reported in Table 2. The largest deviation from ideality is the N1–Mn1–N2 angle of 74.2(1)°, due to the restraints in the chelating bite of this type of ligand, and that falls in the range already observed in similar Mn(II) complexes with polydentate ligands bearing both pyridine (or imidazole) and carboxylate.[17,18,31] The Mn–N_{py} distance in **1** (2.363(5) Å) is the largest reported for similar Mn(II) compounds (2.23–2.32 Å).[17,18,31–36] This can

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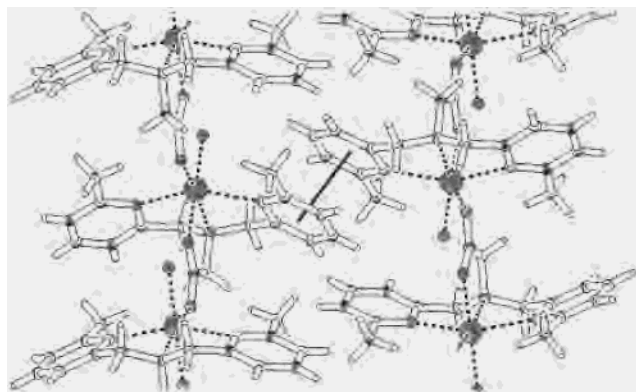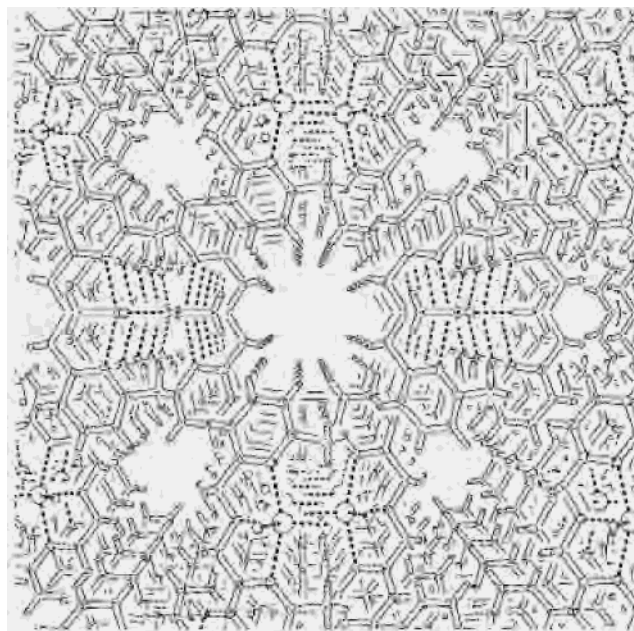
Figure 4. Two adjacent chains running along the *a* axis with the $\pi-\pi$ interaction between the pyridine rings represented by a bold line.

Figure 5. View in the (1 0 0) direction of the structure where the PF_6^- moieties have been omitted to highlight the cavities that host the anionic molecules.

be related to the presence of 6-methyl groups on the pyridine. On the contrary, the Mn–N_1 distance, where N_1 is the tripodal nitrogen, is one of the smallest (2.248(5) Å for **1** with a range from 2.232–2.483 Å for similar compounds).[17,18,31–36]

The bridging carboxylate in the syn-anti conformation as in **1** is rather rare by comparison with syn-syn bridging mode.[2] It is more frequently encountered when the carboxylate is part of a polydentate ligand,[37–40] presumably because of steric congestion.[41] In **1**, as in other reported cases,[16,17,36,42–48] it gives rise to a polymeric compound. The zigzag chain (Figure 4) runs parallel to the unit cell *a* axis with a Mn to Mn distance of 5.564(2) Å. This distance falls in the range [5.28–5.70 Å] for μ-carboxylato syn-anti Mn(II) polynuclear complexes tabulated in table 3. These chains run parallel to each other, and the pyridine moieties form couples of long $\pi-\pi$ interactions with a centroid to centroid distance of 3.72 Å as can be seen from Figure 5. The shortest Mn⋯Mn separation between adjacent chains is 9.062(2) Å.

The striking feature of compound **1** is that, differently from the structures reported in the literature, it has the manganese atoms lying on a symmetry plane and this prevents the

formation of chiral structures as observed by, among others, us[17] and Iikura et al.[31] A further peculiarity of this structure is that the arrangement of these molecules allows the formation of tunnels (Figure 5) that develop parallel to the polymeric chains and that host the anionic PF_6^-. It is noteworthy that the PF_6^- are not disordered in this structure, differently from what have been obtained in the case of **2** (for which two sites with a respective probability of 0.75 and 0.25 were found).

Magnetic Properties. Magnetic susceptibility data were collected on **1** and **3** ground crystals in the temperature region 2–300 K and within an applied field of 10 kG and 0.01 kG, showing no difference. The behavior of both $1/\chi$ and χT as a function of *T* has been fit to numerical solutions derived according to the crystallographic structures (see procedure in the Experimental Section).

Compound 3. The magnetic behavior of **3** is shown in Figure 6, χ_3 being the molar magnetic susceptibility [per two Mn(II)]. At room temperature, the product χT (8.80 cm^3 K mol^{-1}) for **3** corresponds to the value expected for uncoupled Mn(II) ions (respectively 8.75 cm^3 K mol^{-1} for two Mn-(II)). Between 300 and 70 K, χT was constant, and then it decreased to a value of 1.65 cm^3 K mol^{-1} at 2 K.
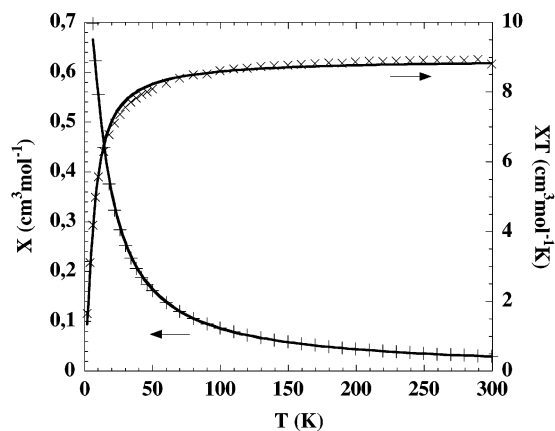
This behavior of the magnetic susceptibility as a function of *T* is indicative of an antiferromagnetic coupling between the two Mn(II) ions. The molar magnetic susceptibility of such a molecular dimer can be reproduced by the following Heisenberg Hamiltonian:

$$\mathcal{H} = -2JS_1 \cdot S_2 \tag{1}$$

The expression of the molar magnetic susceptibility was derived from the field-independent van Vleck equation,[49]

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Figure 6. Thermal variation of χT ($\times$) and χ (+) versus temperature for **3**. For clarity, only 50% of the recorded data is shown. Plain lines correspond to the calculated data with the following parameters: $g = 2.02$, $J/k = -0.69$ K, $\rho = 1.5\%$.
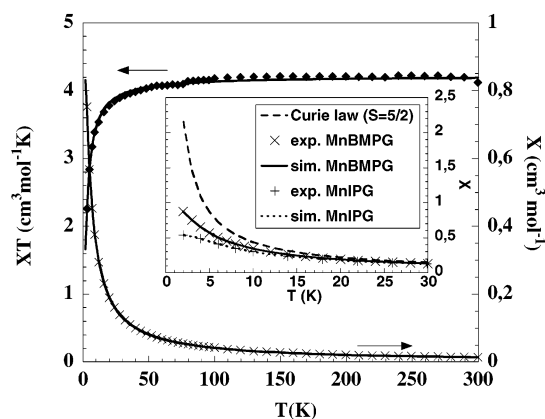
Figure 7. Thermal variation of χ ($\times$) and χT ($\blacklozenge$) for **1**; for clarity, only 50% of the recorded data is shown. The plain lines correspond to the calculated data for **1** for the following parameters: $g = 1.965$, $J/k = -0.172$ K, $zJ'/k = -0.006$ K. Inset: Thermal variation of χ for **1** ($\times$ and plain line), for **2** (+ and dot-line for the calculated data (parameters: $g = 1.970$, $J/k = -0.25$ K, $zJ'/k = -0.11$ K)), and for the Curie law ($g = 2$) (dashed line). MnBMPG stands for **1** and MnIPG for **2**.

including the contribution of a monomeric Mn(II) impurity (ρ) that could have arisen from bridge disrupture.[50] The data were fit using two independent procedures (see Figure 6 and Experimental Section). The best parameters and corresponding uncertainties, consistent with both the two procedures, were $g = 2.020 \pm 0.006$, $J/k = -0.693 \pm 0.016$ K, and $\rho = (1.5 \pm 0.5\%)$ (see Experimental Section).

Compound 1. For both **1** and **2**, at very low temperature, the experimental susceptibility was smaller than that predicted by the Curie law for $S = {}^5/_2$ and $g = 2$ (see Figure 7). This indicates some weak antiferromagnetic coupling between two metallic centers along the chain. **1** displays a weaker coupling as $\chi_1 > \chi_2$ in the whole temperature range [2–300 K]. As previously shown on **2**,[17] the magnetic properties of such $S = {}^5/_2$ chains can be successfully

reproduced using an analytical law derived by Fisher[51–55] from the Heisenberg model. The Hamiltonian used here is

$$\mathcal{H} = -2J\sum_i S_i \cdot S_{i+1} \qquad (2)$$

where J is the exchange coupling between two adjacent paramagnetic centers. The fitting can be improved by taking into account interchain interactions via a mean field, involving an interchain coupling J' with z nearest neighbors.[17,52,56–58] The best parameters (g, J/k, zJ'/k) were $g = 1.965 \pm 0.002$, $J/k = -0.172 \pm 0.005$ K, and $zJ'/k = -0.006 \pm 0.004$ K for **1**. As shown in Figure 7, a good agreement was obtained for **1** in the whole temperature range. The J and J' values obtained are small, and, thus, the precision on their absolute value must be low. Uncertainties were estimated by taking into account the results from two independent fitting procedures (see Experimental Section). The value of the parameter J is more reliable than the zJ' parameter value. However, the order of magnitude for zJ' is meaningful.[59]

The antiferromagnetic coupling along the chain for **1** is of the same order of magnitude as the antiferromagnetic coupling in **2** (1.970, −0.25 K, −0.11K)[17] and at least 1 order of magnitude smaller than those reported for halogenated chains (see Table 3). These small values are due to the syn-anti coordination mode of the carboxylate which is imposing both a long Mn−Mn distance (by comparison to the syn-syn mode, see Table 3) and a mismatch in the orientation of magnetic orbitals (by comparison to both the syn-syn and anti-anti coordination modes).[17,38,58,60–62] A small interchain coupling was obtained for both chains. The shortest Mn−Mn interchain distance for **1** is 9.062(2) Å (respectively 8.42 Å for **2**). In both compounds, two adjacent chains are connected through interactions between aromatic groups from the ligands (pyridine for **1** with a centroid to centroid distance of 3.72 Å, pyridine and imidazole for **2** with a distance of 3.8 Å). As already suggested in the case of **2**, such a $\pi-\pi$ interaction could mediate the interchain coupling.[17]

Magnetic Properties of Carboxylato-Bridged Mn(II) Compounds: Dependence of J on the Nature of the Bridge. The most common feature for carboxylato bridges is the syn-syn mode. The bridges encountered in **1**, **2**, and **3**

(50) It should be noted that the microanalysis for **3** (calcd H 3.78, C 30.01, N 14.58, F 23.74, P 6.45, Mn 11.44; found H 3.66, C 30.43, N 14.61, F 23.38, P 6.88, Mn 11.46) is good (see ref 18). Moreover, we have checked on another close compound involving a Mn(II) and a similar ligand bearing no carboxylate but only imidazoles and found that the contribution to χT is constant down to 2 K (no zero-field splitting effect, as expected for a mononuclear Mn(II)).

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Table 3. Exchange Couplings for Some Mn(II) Carboxylato-Bridged and Halogenato-Bridged Compounds, Corresponding g Values, and Mn−Mn Distances[g]

compound	no.	type	Mn−Mn distance (Å)[a]	bridge	g	J/k [K][b]	ref
Single Carboxylato Bridge							
{[Mn(BPP)(H₂O)(MeCN)]₂, 2(BPh₄)·MeCN}∞	**a**	chain	5.376(4) and 5.282(4)	syn-anti		−0.289	31
[Mn(MCPA)₂(H₂O)₂]∞	**b**	2D polymer	5.40	syn-anti	1.90	−0.432	36
Mn[(IPG)(MeOH)]∞(PF₆)∞	**c**	chain	5.42	syn-anti	1.970	−0.25	17
Mn[(BMPG)(H₂O)]∞(PF₆)∞	**d**	chain	5.564(2)	syn-anti	1.964	−0.172	this work
[{Mn(BIPY)₂(H₂O)}₂(Me₂NCH₂CO₂)][ClO₄]₄·2H₂O	**e**	discrete dimer	5.67	syn-anti	1.970	−0.277	33
Mn[(5-NO₂-SALIMH)(MeOH)(μHCO₂)]∞	**f**	chain	5.98	anti-anti	1.96	−0.36	32
average values			5.654[c]			−0.30[d]	
Double Carboxylato Bridge							
[Mn(HBTC)(PMP)(H₂O)]∞	**g**	chain of dimeric units	3.489 (104.39°)	bis-monatomic	2.0	1.04	71
[Mn(BIG)(H₂O)₂]₂, 2(PF₆)	**h**	discrete dimer	3.672(2) (108.4(2)°, 106.4(4)°)	bis-monatomic	1.970	−0.693	this work
[Mn(BPG)(H₂O)₂]₂, 2(ClO₄)	**i**	discrete dimer	3.712(2) (109.1(3)°, 109.8(3)°)	bis-monatomic	1.912(4)	−0.908	31
[Mn(BPP)(H₂O)₂]₂, 2(BPh₄)·2EtOH·2H₂O	**j**	discrete dimer	3.726(4) (108.9(3)°)	bis-monatomic	1.941(3)	−0.942(4)	31
[Mn(TPA)(O₂CMe)]₂	**k**	discrete dimer	4.145(1)	bis(syn-anti)	1.995	−1.399	35
[Mn₂(BIPY)₄(TA)]∞(2ClO₄)∞	**l**	chain of dimeric units	4.64l	bis(syn-syn)	1.97	−0.97	74
average values			3.749[c]			−0.98[e]	
Triple Carboxylato Bridge							
[Mn₂(PhCOO)₃(MeOH)(BIPY)₂](NO₃)	**m**	discrete dimer	3.498(4) (104.1(3)°)	monatomic bis(syn-syn)		−1.58	34
[Mn₃(MeCOO)₆(BIPY)₂]	**n**	discrete trimer	3.614(1) (112.2°)	monatomic bis(syn-syn)	1.99	−3.17	77
[Mn₂(Ph₂MeCCOO)₃(BIPY)₂](PF₆)	**o**	discrete dimer	3.688	(syn-syn) bis(syn-anti)[f]		−0.29	34
[Mn₂(MeCOO)₃(Me₃TACN)₂](BPh₄)	**p**	discrete dimer	4.034(2)	tris(syn-syn)	2.025	−2.52	78
average values			3.710[c]			−1.89[d]	
Halogeno Chains							
[Me₄N]MnCl₃		chain	3.25	chloro		−6.3	53
CsMnBr₃		chain	3.26	bromo		−9.5	79
CsMnCl₃		chain	4.73	chloro		−3	55

[a] For chains, intrachain distance; for polymers, closest distance; when monatomic bridges are involved, the value of the angle Mn−O−Mn is provided in parentheses. [b] J values reported here correspond to the convention $H = -2JS_aS_b$ for two coupled centers. [c] Average distances for the corresponding type of bridge. [d] Average J values for the corresponding type of bridge. [e] Average J values for the corresponding type of bridge only on the five antiferromagnetically coupled compounds. [f] Close to syn-anti. [g] Abbreviations used in Table 3: BIPY = bipyridine; BIG = N,N-bis[(1-methylimidazol-2-yl)methyl]glycinate; BMPG = N,N-(2-(6-methyl)pyridylmethyl)glycinate; BPG = bis(2-pyridylmethyl)aminoacetate; BPP = 3-(bis(2-pyridylmethyl)amino)propionate; H₃BTC = benzene-1,3,5-tricarboxylic acid; IPG = N,N-(2-pyridylmethyl)((1-methylimidazol-2-yl)methyl)glycinate; Me₃TACN = N,N',N''-trimethyl-1,4,7-triazacyclononane; MCPA = 2-methyl-4-chlorophenoxyacetic acid; PMP = pyridyl-2-(1-methyl-1*H*-pyrazol-3-yl); SALIMH = 4-(2-((5-nitrosalicylidene)-amino)ethyl)imidazole; TA = terephthalate; TPA = trispyridylamine.

are rather rare, both because they are of low multiplicity (respectively single, single, and double bridges) and because of the peculiar conformation of the bridges. The μ-η^1-carboxylato, found in **3**, although common in copper(II) polynuclear complexes,[2,63−68] has been much less frequently reported with other metals.[9,16,69−72] An unsupported syn-anti carboxylato bridge between Mn(II), as found in **2** and **1**, is not very common,[9,17,31,33,35,36,44−48,73] and only in a few cases,[9,17,31,33,36] the magnetic properties have been reported so far.

The J values of complexes **1**, **2**, and **3** as well as those of some other reported Mn(II) discrete complexes or polymers with carboxylato bridges are compiled in Table 3. The J values are provided in K (J/k), and they all correspond to

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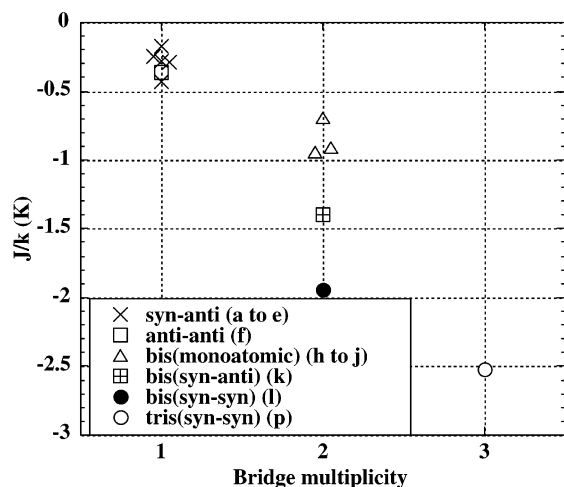
Figure 8. Antiferromagnetic couplings (*J*/*k*) from Table 3 versus bridge multiplicity. Only complexes involving one type of bridge are considered. The legend specifies the bridging mode and the label of the corresponding compound in Table 3.

the convention $\mathscr{H} = -2JS_aS_b$ for the interaction between two coupled centers. For the sake of comparison, *J* values of some halogenato Mn(II) chains are also provided. For complexes involving carboxylato bridges, we have restricted the data to Mn(II) complexes involving only carboxylato bridges but with several multiplicities (single, double, or triple bridge) and several geometries. The exchange coupling through carboxylato bridges has been shown, mainly on dicopper(II) complexes, to be dependent both on the number of bridges involved and on the bridge geometry.[6,17,31,38,39,58,60−62,74−76] *J* values are smaller for dimanganese(II) compounds ($J = (1/(n_A n_B))\sum j_{\mu\nu}$, where the sum goes all over the exchange pathways with one major pathway for each bridge and $n_A = n_B = 5$ for di-Mn(II)), but a similar dependence is expected, as one $j_{\mu\nu}$ must be dominant for each bridge. The comparison of data from Table 3, far from definitive, was just made to stress this dependence and shed some more light on structural−magnetic correlations for such compounds. It would have to be reconsidered when more data will be available in the literature on only carboxylato-bridged Mn(II) compounds.

Polynuclear manganese(II) complexes from Table 3, bridged by 1, 2, or 3 carboxylato groups, show a weak coupling which is usually antiferromagnetic (*J* < 0), except for one compound (**g**). The antiferromagnetic couplings through carboxylates are weaker than that reported for halogenated Mn(II) chains. They vary from −0.17 to −3.17 K, which is more than 1 order of magnitude. The variation is related to the number of bridges and to the bridge geometry. Antiferromagnetic couplings *J*/*k* versus bridge multiplicities are plotted in Figure 8.

(i) Bridge Multiplicity. To avoid any effect that could arise from countercomplementarity,[52] only compounds in-

volving one type of carboxylato bridge have been considered in Figure 8. A general trend can be derived from this figure. The magnitude of |*J*| increases with the number of carboxylato bridges, as previously published.[31,36]

This general trend can be related both to increasing number of pathways for superexchange, as far as no countercomplementarity is encountered, and to reduced internuclear distances with increasing bridge multiplicity (see average distances in Table 3).

(ii) Bridging Mode. Within a set of compounds with the same bridge multiplicity, the magnitude of the coupling depends on the bridging mode. The syn-syn mode is known to induce larger |*J*| than the other triatomic bridges.[6,17,31,38,39,58,60,61,62,74−76] This general trend applies in this Mn(II) series.

It is worth noting that the syn-syn is a particularly efficient pathway for superexchange, even by comparison with the [(*μ*-*η*¹-carboxylato)] bridge. Despite longer intermetallic distances, the triatomic (−OCO−) syn-syn mode induces |*J*| values comparable to or even greater than the monatomic (−O−) [(*μ*-*η*¹-carboxylato)] bridge (see **h**, **i**, and **j** (bis-monatomic) versus **l** (bis(syn-syn)) or **m** and **n** (monatomic-bis(syn-syn)) versus **p** (tris(syn-syn))).

To conclude with that comparison, the magnitude of the antiferromagnetic coupling mediated through carboxylato bridges (|*J*|) increases with the number of bridges. The syn-syn mode is an efficient pathway, even by comparison with the [(*μ*-*η*¹-carboxylato)] mode.

Conclusion

In this article, we have reported structural and magnetic properties of a polymeric Mn(II) compound involving monocarboxylato syn-anti bridges (**1**), the polymer arising from repetition of the unit [Mn−O−C−O−]. The structure of compound **1** is of current interest because of the tridimensional array that displays long channels running parallel to the polymeric chain and hosting anion PF_6^-. The tridimensional structure arises from noncovalent interactions, metal coordination between Mn(II) and carboxylates that creates a 1D polymer, and $\pi-\pi$ interactions between pyridines that organize the chains parallel to each other.

The magnetic properties of this infinite chain have been compared to a closely related compound (**2**).[17] The magnetic properties of a dimeric Mn(II)Mn(II) compound previously isolated from a closely related ligand[18] have also been described here. They were compared to a series of Mn(II) complexes of different nuclearities with bridging carboxylates in several modes. The exchange coupling through carboxylato bridges is usually weak and antiferromagnetic. It is dependent both on the number of bridges involved and on the bridge conformation, as described in the literature, mainly for copper(II) compounds.[6,17,31,38,39,58,60−62,74−76] The magni-

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tude of the interaction ($|J|$) increases with the number of bridges. The syn-syn bridge is an efficient pathway, even by comparison with the monatomic[($\mu\text{-}\eta^1$-carboxylato)] bridge.

Compounds **1**, **2**, and **3** are interesting from a reactivity point of view. They are soluble in several solvents, indicating a disrupture of the bridge structure, providing a monomeric compound with an open shell.[18] The initial goal was to mimic the active site of manganese superoxide-dismutases,[18] and we are currently studying their reactivity toward superoxide. As they bear respectively zero (**2**), one (**1**), and two (**3**) water molecule(s) on the manganese(II) center, they are of much interest to test the reactivity and to address the role of coordinated water.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026130L

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