An Inorganic Helix $[Mn(IPG)(MeOH)]_n[PF6]_n$[‡]: Structural and Magnetic Properties of a *syn-anti* Carboxylate-Bridged Manganese(II) Chain Involving a Tetradentate Ligand

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The crystal structure of an infinite inorganic chain consisting of Mn^{II} and an *N*-centered tripodal ligand *N*,*N*-(2-pyridylmethyl)[(1-methylimidazol-2-yl)-methyl]glycinate is presented. It exhibits a chiral helical structure with a pitch of two monomeric units (each monomeric unit containing one Mn atom). Each manganese is connected to its neighbor through a carboxylate bridge in a *syn-anti* geometry. Around each manganese center, two carboxylates bind in a *cis* geometry. This peculiar bridging geometry (*syn-anti cis*) provides a broken-line chain, running in a zig-zag manner along the *b* axis of the $P2_1$ space group. The magnetic properties have been investigated. They show a pseudo-2D magnetic structure, with one major pathway along the chain and an inter-chain minor one. The intrachain coupling is a weak antiferromagnetic interaction (J/k = –0.25). This low value is entirely consistent with the geometry of the bridge. The interchain coupling is a weaker antiferromagnetic coupling (J′/k = –0.11) and could be mediated through π-π interactions between pyridine and imidazole from two adjacent helixes.

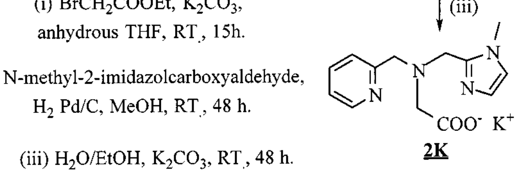
Introduction

Carboxylate ligands play an important role in coordination chemistry. They are known to adopt binding modes as diverse as terminal monodentate, chelating to one metal center and bridging bidentate in a *syn-syn*, *syn-anti* or *anti-anti* configuration to two metal centers. The *syn-anti* bridge appears to be a rather uncommon binding mode.[1][2] In the past fifteen years, there has been a flow of interest in carboxylate complexes as models for metalloproteins. The carboxylate can be incorporated as an external ligand, usually as an acetate. However, in the metallic cores of metalloproteins, the carboxylato ligand is provided by the side chain of an aspartate or a glutamate making polydentate chelating ligands bearing a carboxylate and some other donor biologically relevant.[2][3] We have prepared several nitrogen-centered tripodal ligands with three appended moities, one being a carboxylate. Mononuclear iron complexes have previously been obtained and described with a monodentate carboxylate. They have been studied as models for nonheme enzymes.[4][5] Surprisingly, with one of these ligands, *N*,*N*-(2-pyridylmethyl)[(1-methylimidazol-2-yl)-methyl)]glycinate (IPG)[6] **(2)**, Mn^{II} forms infinite chains through carboxylato-bridges in a *syn-anti* geometry. Here, the results of structural and magnetic susceptibility studies on these Mn^{II} chains are described.

Results

Synthesis

Ligand Synthesis – A given tripod can be synthesized by several different methods depending on the order chosen for the introduction of the different moieties. Several strategies were investigated and we report here the higher yield one. In the synthesis of a nitrogen-centered tripod, the yield-limiting step is usually the tertiarization of the amine. Here, the first step is an *N*-alkylation of a primary amine to give a secondary amine which is easily purified by distillation. This compound then reacts quantitatively with an aldehyde by reductive amination. The overall yield is 70% (see Scheme 1). If the first two steps are switched, the overall yield drops to 35% due to the poor yield of the last step (less than 40%).



Scheme 1. IPGK (2K) synthesis

Complex Preparation – To prevent pollution by particules of MnO_2 in the course of the preparation of the Mn^{II}

[‡] IPG: *N*,*N*-(2-pyridylmethyl)[(1-methylimidazol-2-yl)-methyl)]-glycinate

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complex, the ligand was used as a mixture of the potassium salt and the free acid (**2K/2H** mixture) with a pH controlled ratio (see Experimental Section). Crystals suitable for an X-ray diffraction study were grown from a methanol solution.

Description of the Structure

An X-ray diffraction study was carried out on complex **3**. Experimental details are reported in the Experimental Section (Table 1). The crystal structure has been found to consist of a polymeric sequence of Mn^{II} cations, bridged by *syn-anti* carboxylato groups. The charge of the $[\{Mn^{II}IPG(MeOH)\}^{+}]_n$ chain is balanced by n (PF_6^{-}) anions. The polymeric chain extends along the *b* axis of the $P2_1$ chiral space group. An ORTEP representation of a succession of three monomeric units is shown in Figure 1. The three units are labeled 0 for the central one, corresponding to the crystallographic unit [*x, y, z*], −1 and +1 for the two adjacent ones along the chain, with the symmetry transformations $[-x, -0.5 + y, 1 - z]$ and $[-x, 0.5 + y, 1 - z]$ respectively. Selected bond lengths and angles are presented in Table 2.

Mn^{II} is hexacoordinated with a pseudo-octahedral environment. Four of the donors are provided by the ligand **2**, through the imidazole nitrogen N1A, the pyridine nitrogen N1B, the tripodal nitrogen N and one carboxylato oxygen O2. The fifth donor is provided by the carboxylato oxygen O1 from the carboxylato of unit (−1). The final coordination site is filled by a molecule of methanol. The $Mn-N_{tripodal}$ distance [2.35(3) Å] is longer than the other Mn−N bonds, but shorter than the corresponding sum of the van der Waals radii (2.82 Å), indicating that the metal is hexacoordinated. The Mn−N1A distance [2.13(2) Å] is significantly shorter than the Mn−N1B distance [2.23(2) Å], suggesting a stronger bond with the imidazole ligand. Such small $Mn-N_{imidazole}$ distances were reported to be characteristic of bridged structures.[7] Imidazole and pyridine are in the trans positions with regard to Mn and the two aromatic rings are parallel to each other [Φ = 5(1)°]. The Mn atom and the three oxygens O1, O2′ and O3 (see Figure 1) (carboxylate and methanol) are coplanar (mean

Table 1. Crystallographic data for **3**

Formula	$C_{14}H_{19}F_6MnN_4O_3P$
Formula weight	491.24
Temperature [K]	293(2)
Wavelength [Å]	0.71073
crystal system	monoclinic
space group	$P2_1$
a [Å]	8.417(4)
b [Å]	9.626(5)
c [Å]	12.391(6)
α [°]	90
β [°]	92.61(5)
γ [°]	90
V [Å³]	1002.9(9)
Z	2
d_{calc} [g.cm^{-3}]	1.627
abs. coeff. [mm^{-1}]	0.815
crystal size [mm]	0.200 × 0.150 × 0.070
collected reflections	568
independent reflections	531 [R(int) = 0.0264]
data/restraints/para	531/43/149
goodness-of-fit on F^2	1.068
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0545, wR2 = 0.1361$[a]
R indices [all data]	$R1 = 0.0587, wR2 = 0.1425$
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ [e.Å^{-3}]	−0.313 and 0.319

[a] Weighting scheme: $w = 1/[s^2(F_o^2) + (0.0776P)^2 + 8.47P]$ where $P = (F_o^2 + 2F_c^2)/3$.

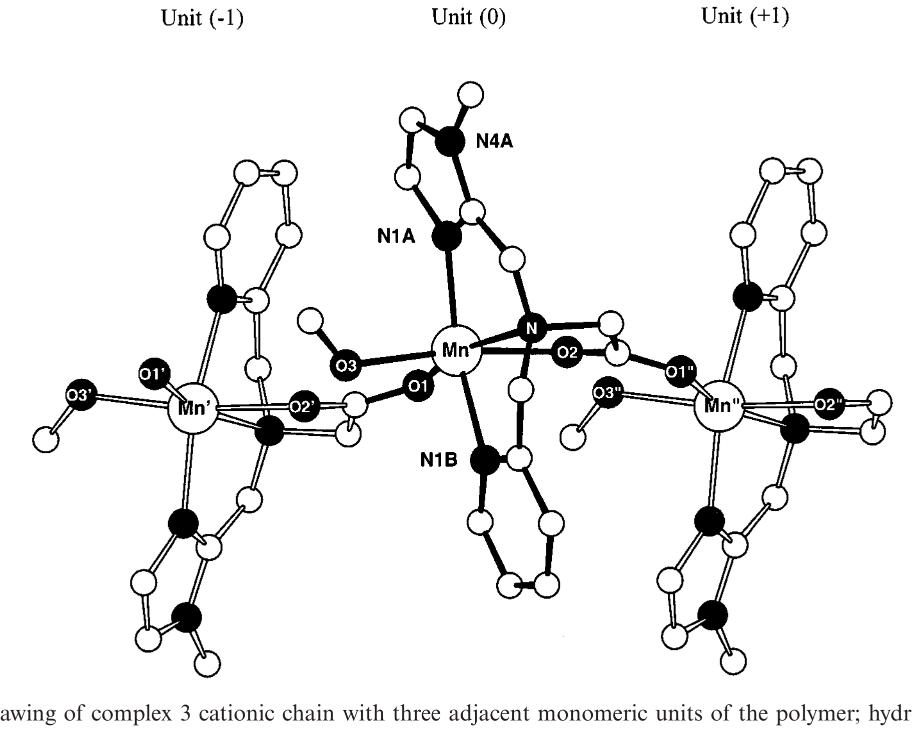

Figure 1. ORTEP drawing of complex 3 cationic chain with three adjacent monomeric units of the polymer; hydrogen atoms have been omitted for clarity

Table 2. Selected bond lengths [Å] and angles [°] for **3**

Mn−N(1A)	2.13(2)	O(1)−Mn−N(1B)	98.2(6)
Mn−O(1)	2.13(2)	O(2)−Mn−N(1B)	84.7(6)
Mn−O(2)	2.18(2)	N(1A)−Mn−O(3)	88.4(7)
Mn−N(1B)	2.23(2)	O(1)−Mn−O(3)	92.5(6)
Mn−O(3)	2.26(2)	O(2)−Mn−O(3)	171.8(5)
Mn−N	2.36(2)	N(1B)−Mn−O(3)	87.2(6)
		N(1A)−Mn−N	75.7(6)
N(1A)−Mn−O(1)	114.1(6)	O(1)−Mn−N	162.4(6)
N(1A)−Mn−O(2)	98.8(7)	O(2)−Mn−N	75.5(6)
O(1)−Mn−O(2)	88.3(6)	N(1B)−Mn−N	74.0(6)
N(1A)−Mn−N(1B)	147.5(6)	O(3)−Mn−N	102.7(6)

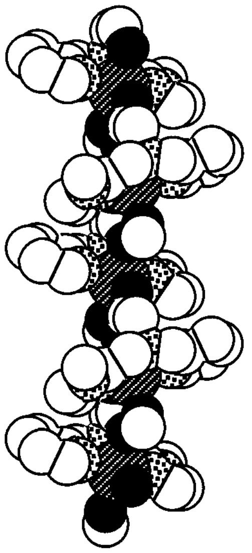

Figure 2. View of the helicoïdal organisation with space filling representation

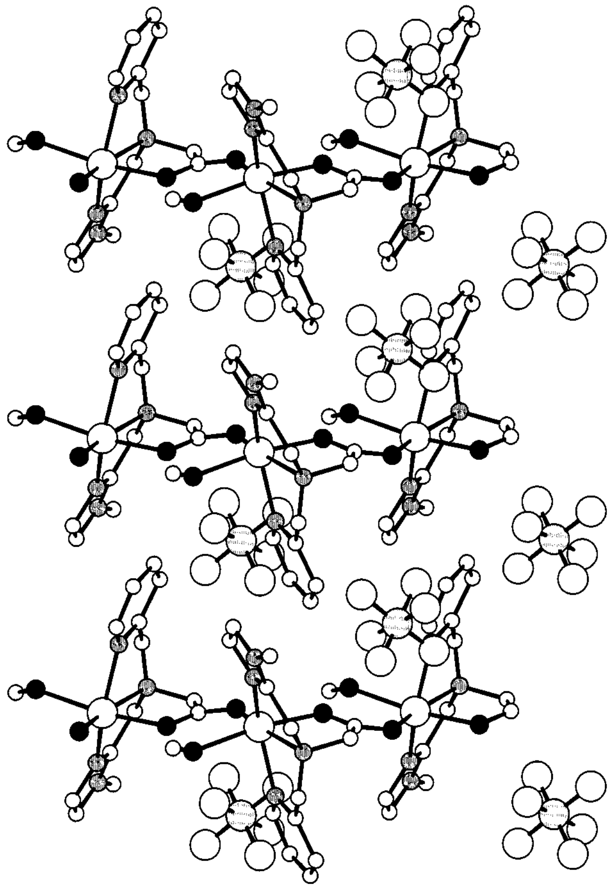

Figure 3. ORTEP packing diagram; the disorder of the anionic units has been omitted for clarity

displacement 0.006 Å), the tripodal nitrogen N being located at 0.34(2) Å from this mean plane.

The carboxylates bridge two mononuclear units with a *syn-anti* pattern, forming an infinite chain. The manganese from unit 0 is slightly closer to the carboxylato oxygen O1 belonging to a ligand from the adjacent unit (−1) than to O2 [see Figure 1; 2.13(2) Å (Mn−O1) versus 2.18(2) Å (Mn−O2)]. O1 interacts with the manganese through its *syn* lone pair and O2 through its *anti* lone pair. All distances and angles (see Table 2) are consistent with those previously found in manganese *syn-anti* μ-carboxylato systems.[8−16] Although the H-atom of the coordinated methanol could not be located on difference Fourier-syntheses, it seems clear that a strong internal hydrogen bond occurs between the acceptor oxygen O2 of the carboxylate group and the oxygen donor of the methanol of the adjacent unit +1 [see Figure 1; *d*(O2−O3″) = 2.63(2) Å]. This hydrogen bond involves the *syn* lone pair of O2.

The two oxygens O1 and O2 are in a *cis* conformation with regard to Mn, with a (O1−Mn−O2) angle of 88.3(6)°. The chain develops in a zig-zag manner, with an ($Mn_{-1}-Mn_0-Mn_{+1}$) angle of 125.3° and a nonplanar Mn−O−C−O−Mn pattern. From unit −1 to unit 0, the plane of the two aromatic rings is tipped over by 64° (see Figure 2). The third unit along the chain can be deduced from the first one by translation (10.84 Å). The structure can be described as a chiral helix-like chain running parallel to the *b* axis and with a pitch of two complexes (see Figure 2). The Mn−Mn distance is 5.42 Å and is in the typical range which has previously been described for such *syn-anti* bridges between Mn^{II} [5.2−5.8 Å].[9−16]

The spatial arrangement of the complex **3** is displayed in Figure 3. The packing diagram reveals a layer organisation with entangled parallel helixes. A pyridine moiety from one helix is parallel to an imidazole from the next, with a small interplanar distance (3.8 Å). The closest distance between two Mn from two adjacent helixes is 8.42 Å.

Magnetic Properties

The results of susceptibility measurements are shown in Figure 4. At very low temperature, the experimental susceptibility is smaller than that predicted by a Curie law for S = 5/2 and g = 2 (see inset, dash line). This indicates some small antiferromagnetic coupling between two metallic centers in **3**. The magnetic properties of such a chain can be explained by the Heisenberg linear-chain model. The Hamiltonian used here is:

$$\boldsymbol{H} = -2\,J \sum_{i} S_i \cdot S_{i+1}$$

where the summation is all along the chain and J is the exchange coupling between two adjacent paramagnetic centers. An analytical law has been derived by Fisher for infinite chains and large spins.[17][18] For an infinite S = 5/2 chain, the expression of the chain molar magnetic susceptibility χ_c is:[19–21]

$$\chi_c = (35/32)*(1/T)*g^2(1+u)/(1-u)$$

$$\text{with } u = \coth[(35/32)*(1/T)*(J/k)]-[(2/35)*T*(k/J)]$$

Fitting the data to that expression provided an estimate of J (J/k = −0.27). However, the g value thus obtained was too small for a Mn^{II} high spin complex (g = 1.946, with an agreement factor for the fitting $R = 1.51 \times 10^{-4}$). The fitting was improved by taking into account interchain interactions via a mean-field.[18][22] The expression used to fit the data was:

$$\chi = \frac{\chi_c}{1-\dfrac{2zJ'\chi_c}{Ng^2\beta^2}} = \frac{\chi_c}{1-\dfrac{16}{3}\,z\,\dfrac{J'}{k}\,\chi_c}$$

where J′ is the interchain-exchange coupling and z the number of nearest neighbors. The best fit of Equation 2 in the temperature range 2−300 K was found for J/k = −0.25 ($-0.17\ cm^{-1}$), zJ′/k = −0.11 ($-0.078\ cm^{-1}$) and g = 1.970 with an agreement factor $R = 2.17 \times 10^{-5}$. All three parameters were allowed to vary during the fitting process. As can be seen in Figure 4, the experimental points and theoretical curve are superimposed in all the temperature range. The J and J′ values obtained are very small and thus the precision on their absolute value must be rather low. Moreover the ratio zJ′/J = 0.4 is at the high limit for the mean-field model to be valid.[22–24] This increases the uncertainty on J′ although the order of magnitude both for J and J′ is still meaningful.

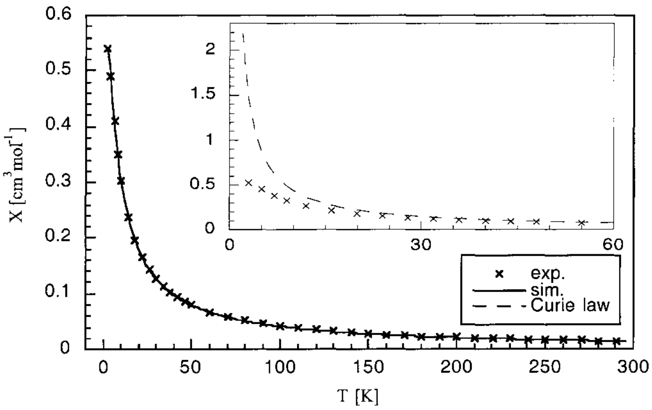

Figure 4. Experimental and calculated temperature dependences of χT; for clarity only 50% of the experimental points are shown; the dashed line was generated with a Curie law for S = 5/2 and g = 2 (see text); the solid line is the best fit obtained including the mean-field correction (see text for parameters)

Discussion

A *syn-anti* bridging configuration is rare by comparison with a *syn-syn* configuration.[2] The former is made easier by steric congestion[25][26] and is more frequently found when the carboxylate is part of a polydentate ligand[27–30] or a substituted acetate,[13,15,16,25] including amino acids.[14][31] It has been reported for discrete complexes,[15] polymeric chains and networks with manganese.[9–14,16,31]

The main structural feature of compound **3** is the chiral helix-like structure with a nonlinear bridging network. This is due both to the *syn-anti* bridging mode of the carboxylato ligand and to the *cis* position of the two oxygens O1 and O2 in the octahedron around Mn. IR spectroscopic data are consistent with a bridging carboxylate and not a unidentate one: the small value of $\Delta\nu = (\nu_{asCO}) - (\nu_{sCO}) = 131 cm^{-1}$ is characteristic of a bridging carboxylate.[1] Another important feature is the layer organisation. In the crystal packing, the chains are stacked by π-interactions with an interplanar spacing of 3.8 Å between the pyridine from one helix and the imidazole from the next.

Very little is known about the magnetic properties of such carboxylato *syn-anti* manganese chains. On the contrary, the magnetic properties of manganese chains involving halogen bridges have been extensively described and are classical examples of linear chain compounds (see Table 3).[19–21,32] The carboxylato *syn-anti* bridge has received some attention because it allows a large variety of structural and magnetic features.[23,29,33] Without being exhaustive, the magnetic behavior has been studied for *syn-anti* carboxylato bridges in chain structures involving homonuclear[23,28,29,33–35] Cu^{II}, heterodinuclear[36] Mn^{II} and Cu^{II} or in discrete complexes[27] (Fe^{III}). The magnetic properties have also been studied for a 2D-polymer with a *syn-anti* carboxylato network[16] between Mn^{II}, and on a discrete Mn^{II} homodimer involving a mono *syn-anti* carboxylato bridge (see Table 3).[15]

The intrachain coupling constant in compound **3** is at least one order of magnitude smaller than that reported for halogenated Mn^{II} chains (see Table 3). The exchange coupling through the carboxylato moiety is highly dependent on the conformation of the bridge between the metal centers that are interacting.[18,34,37] A *syn-syn* pattern provides small metal−metal distances and a good overlap of magnetic orbitals. It induces high antiferromagnetic coupling, as has previously been reported in $Cu_2(CH_3COO)4{\cdot}2H2O$ where the four acetates are in a *syn-syn* configuration with J = $-150\ cm^{-1}$.[38][39] *Syn-anti* carboxylato bridges induce much smaller J values because of the expanded metallic core and a mismatch in the orientation of magnetic orbitals.[23,29,34,36] For compound **3**, the Mn−Mn intrachain distance is 5.42 Å, which is rather large. Moreover, the bridging network displays a “zig-zag” structure (see description of the structure). To the best of our knowledge, there are considerably fewer examples involving two carboxylato *syn-anti* ligands in a *cis* position than in a *trans* position. The four closest structures, studied from a magnetic point of view, found in the literature are: (a)[29] and

Table 3. Antiferromagnetic couplings for several Mn^{II} compounds (including chains, one 2D-polymer and one dimer) and related Mn−Mn distances

Compound	Mn−Mn distance[c] [Å]	Bridge	J [K]	ref.
$[(CH_3)_4N]MnCl_3$	3.25	Chloro	−6.3	[20]
$CsMnBr_3$	3.26	Bromo	−9.5	[32]
$CsMnCl_3$	4.73	Chloro	−3	[19]
Mn[(5-NO$_2$-salimH)MeOH(μ-HCO$_2$)][a]	5.92	Carboxylato *anti-anti*	−0.36	[7]
Mn[(MCPA)$_2$(H$_2$O)$_2$]$_n$[b]	5.40	Carboxylato *syn-anti*	−0.3 to −0.4	[16]
Mn[(bipy)$_2$(H$_2$O)$_2$(Me$_2$N CH$_2$CO$_2$)][ClO$_4$]·2H$_2$O	5.67	Carboxylato *syn-anti*	−0.27	[15]
3	5.42	Carboxylato *syn-anti*	−0.25	this work

[a] 5-NO$_2$-salimH = 4-(2-[(5-nitrosalicylidene)amino)ethyl]imidazole. − [b] MCPA = 2-methyl-4-chlorophenoxyacetic acid. − [c] For chains, intrachain distance; for polymer, closest distance.

(b)[40][41] two copper(II) chains, (c) a copper tetranuclear cluster[28] and (d) a copper(II) ladder-like chain of dimer units with a di-μ-carboxylato.[35] Both (a) and (b) show a helix-like structure that bears a great number of structural similarities with compound **3** with a ferromagnetic coupling J/k = 2.4 and J/k = 4.0, respectively. Compound (c) also displays a ferromagnetic coupling J/k = 3.8. In compound (d), a very small antiferromagnetic coupling was estimated at −0.7 K.

The importance of the *syn-anti* conformation on the magnitude of J has previously been stressed for copper(II) compounds.[28−30] It can also be illustrated for compound **3** by some relevant comparisons. First, two structures with *syn-anti* carboxylato bridges between Mn^{II} have previously been reported and studied from a magnetic point of view: (e) a 2D-polymer[16] containing a *syn-anti* carboxylato lozenge-shaped network between Mn^{II} and (f) a discrete Mn^{II} dimer involving a mono *syn-anti* carboxylato bridge.[15] In (e), the Mn−Mn distance is 5.40 Å and an antiferromagnetic coupling J/k of −0.3 to −0.4 was estimated. In (f), the intermetallic distance is 5.67 Å with an antiferromagnetic coupling J/k = −0.27. These exchange coupling constants are of the same order and are very close to that obtained for compound **3**.[42] Another comparison can be made with a Mn^{II} chain with a dipodal *N*-centered ligand bearing one imidazole and one phenolate involving a formate bridge in a *anti-anti cis* binding mode (see Table 3).[7] The Mn−Mn distance along the chain is 5.92 Å and J/k = −0.36. Despite a larger distance, the antiferromagnetic coupling is greater than in compounds **3** and (f).[43] Presumably this is related to the *anti-anti* pattern inducing better orbital overlap.[30] The geometric characteristics of **3** (*syn-anti* carboxylato bridges, "zig-zag" structure with nonplanar Mn−O−C−-O−Mn pattern) account for the very low value determined for the intrachain coupling constant (J/k = −0.25).

The value of the ratio zJ′/J = 0.4 suggests a pseudo-2D magnetic structure. The shortest Mn−Mn interchain distance is 8.42 Å, each Mn having two closest neighbors (*z* = 2). Two adjacent helixes seem to be connected through π-π interactions between a pyridine moiety and the imidazole group (see Figure 3). Despite the large Mn−Mn interchain distance (8.42 Å), a π-π interaction provides an effective pathway for interchain exchange interaction.

Conclusions

In this article, we have reported the structure and magnetic study of a polymeric Mn^{II} compound involving carboxylato *syn-anti cis* bridges. The compound described here is of interest for several reasons. First, it involves a carboxylato bridge that is part of a polydentate ligand and not a separate acetate. This carboxylate has been shown to be coordinated to the Mn^{II} centers in a *syn-anti* mode, affording a chiral helix-like polymeric structure. It also displays a pseudo-2D magnetic structure with a weak exchange interaction through intrachain *syn-anti cis* carboxylato bridges and a weaker interaction through interchain π-interactions. Finally, it presents a potentially open-shell. The ligand **2** is tetradentate. In the solid state, the coordination sphere of each Mn^{II} center of compound **3** is completed by a molecule of methanol and an oxygen atom (O1) from a carboxylato group from a neighboring molecule of **2**. Compound **3** is soluble in several solvents, indicating a disrupture of the polymeric structure. This probably occurs by the replacement of O1 by a further solvent molecule,[7][44] thus keeping the usual octahedral environment of Mn^{II} complexes. In solution, this compound thus bears two labile coordination sites available for substrate binding. Its reactivity towards superoxide is now under investigation.

Experimental Section

General: IR spectra (KBr) were recorded on a Bruker IFS 66 FT-IR spectrometer. ^{1}H NMR spectra were recorded on Brüker AM 200 and AM 250 spectrometers. X-band electron paramagnetic resonance (EPR) was recorded on a Bruker ER 200E spectrometer. Variable temperature magnetization measurements were collected on ground crystals with a Quantum Design SQUID magnetometer at a magnetic field of 1 T within the temperature range 300−2 K. Data were corrected for diamagnetism of the ligand estimated to -2.431500×10^{-4} cm^3·mol^{-1} from Pascal′s constant.[48] Chemical reagents were purchased either from Aldrich or Acros and used without further purification.

Synthesis and Characterization

***N*-(2-pyridylmethyl)aminoethyl acetate (1):** To a solution of 2-aminomethylpyridine (18.38 g) in 100 mL of anhydrous THF at 0°C, ethylbromoacetate (14.19 g) in 100 mL of anhydrous THF was added dropwise. The reaction mixture was left for 30 min. at 0°C and then allowed to warm to room temperature. After 15 h, the solution was filtered and the filtrate evaporated to dryness. The residual oil was distilled under reduced pressure (0.4 Torr, 100°C), to give a colorless liquid. Yield: 75%. – ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, 3 H, CH_3), 2.81 (s, 1 H, NH), 3.48 (s, 2 H, N$-$*CH$_2$*$-$COOEt), 3.96 (s, 2 H, py$-$*CH$_2$*$-$N), 4.20 (q, 2 H, O$-$*CH$_2$*), 7.17 (t, 1 H, H_{py}), 7.33 (d, 1 H, H_{py}), 7.64 (t, 1 H, H_{py}), 8.56 (d, 1 H, H_{py}).

Potassium *N,N*-[2-pyridylmethyl)(1-methylimidazol-2-yl)-methyl]-glycinate (2K): A solution of **1** (3.88 g) and *N*-methyl-2-imidazolcarboxaldehyde[45] (2.2 g) in MeOH (100 mL) was hydrogenated over (Pd/C, 10%) for 24 h. After filtration and evaporation to dryness, **2K** was obtained by hydrolysis at room temperature in H_2O/EtOH (3:1) with K_2CO_3 (2.2 equiv.) for 48 h. Residual potassium salts were partially removed by extracting the carboxylate **2K** with anhydrous MeOH. Compound **2K** was recrystallized from MeOH/EtOEt. Yield: 95%. – ^{1}H NMR (CD_3OD): δ = 2.95 (s, 2 H, N$-$*CH$_2$*COOK), 3.30 (s, 3 H, CH_3), 3.52 and 3.57 (2s, 2 × 2 H, N$-$*CH$_2$*$-$py and N$-$*CH$_2$*$-$Im), 6.54 and 6.64 (2s, 2 × 1 H, H_{Im}), 7.03 (t, 1 H, H_{py}), 7.14 (d, 1 H, H_{py}), 7.52 (t, 1 H, H_{py}), 8.15 (d, 1 H, H_{py}). – IR (KBr): $\tilde{\nu}$ = 1591 (ν_{asCO}), 1396 (ν_{sCO}), 771 ($\nu_{pyr.\ deform.}$), 742 ($\nu_{imid.\ deform.}$) cm^{-1} (strong bands only).

[Mn(IPG)(MeOH)]$_n$(PF$_6$)$_n$ (3): The pH of a 2×10^{-3} M solution of **2K** in water was adjusted by HCl addition in the 8–8.5 range. After evaporation, the solid was dried under reduced pressure for one night in the presence of P_2O_5 and KCl was removed by extraction of the ligand in anhydrous methanol. Typically, chain crystals were obtained as followed. $MnBr_2$ (330 mg) in deoxygenated MeOH (20 mL) was added to a solution of the ligand (400 mg) in deoxygenated MeOH (20 mL). It was allowed to stand for two hours at 40°C. Then, after cooling, a deoxygenated solution of NH_4PF_6 (3 equivalents) in MeOH (40 mL) was added dropwise. The solution was allowed to stand for a week during which time crystals were formed. Yield: 50%. – $C_{14}H_{19}F_6MnN_4O_3P$ (491.2): calcd C 34.2, H 3.9, N 11.4, P 6.3, Mn 11.2; found C 33.9, H 3.8, N 11.3, P 5.9, Mn 10.6. – IR (KBr): $\tilde{\nu}$ = 1606 (sh), 1571 (ν_{asCO}), 1440 (ν_{sCO}), 770 ($\nu_{pyr.\ deform.}$) 755 ($\nu_{imid.\ deform.}$) cm^{-1} (strong bands only). – The EPR spectrum was recorded on ground crystals at room temperature and 100 K. It shows a broad signal centered at g = 1.98, with no resolved hyperfine structure.

All measurements were performed with crystals or ground crystals from the same batch of crystallization.

Crystal Data, Data Collection and Refinement

Several crystals were tested for their suitability for X-ray diffraction studies. Most of them were twinned. A very thin fragment was found to be a single crystal. This pale yellow-pink crystal of 0.2 × 0.15 × 0.07 mm was mounted on an Enraf–Nonius Cad 4 diffractometer with graphite monochromated Mo-K_α radiation [λ = 0.7107Å]. The unit cell dimensions were refined from setting angles of 25 reflections [$5.2 < \Theta < 11.6°$]. Structure determination and refinement data are reported in Table 1. Data collection was performed at room temperature with $\Theta-2\Theta$ scan technique mode, in the 2Θ range from 4 to 32°. Three standard reflections were measured every hour, to monitor instrument and crystal stability. A 28% decay was observed. A total of 568 reflections was collected [$-6 \le h \le 6$; $0 \le k \le 7$; $0 \le l \le 9$]. From 531 independent reflections, 509 were used [$I > 2\sigma(I)$]. These data were corrected for Lorentz and polarization factors but not for absorption factors.

The structure was solved by direct methods (program SHELXS86)[46] and refined on F^2 for all reflections by least-squares method using SHELXL-93.[47] Hydrogen atoms were calculated and included in the refinement at their ideal positions ($C-H_{ar}$ = 0.93Å, $C-H_{Me}$ = 0.96Å) with an isotropic thermal parameter of 1.2 for the bonded atoms. Only the manganese atom was refined anisotropically to limit the number of parameters versus the number of data.

The asymmetric unit consists of one monomeric complex cation and one counteranion (PF_6). The latter shows disorder; two different sites were found on a difference Fourier-syntheses. A better convergence was obtained with an occupancy factor of 50% and refinement was pursued with restraints. A selection of bond lengths and angles is presented in Table 2 and the crystallographic number scheme is presented in Figure 1 which shows three adjacent units along the axis *b*.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-125980. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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