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Synthesis, Crystal Structure, and Magnetic Properties of Two Manganese(II) Polymers Bearing Ferrocenecarboxylato Ligands

Zilu Chen,[a] Yunsheng Ma,[a] Fupei Liang,*[a] and Zhaohui Zhou[b]

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Reactions of $Mn(ClO_4)_2{\cdot}6H_2O$ with $FcCO_2Na$ [Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$] in methanol solution gave $[Mn_3(FcCO_2)_6(CH_3OH)_4]_n$ (**1**), and, in the presence of 4,4′-bipyridine (4,4′-bpy), $[Mn_3(FcCO_2)_6(H_2O)_2(4,4'\text{-bpy})]_n$ (**2**). Both complexes have the similar chains with a sequence of $\text{–Mn–}(\mu_2\text{-COO})_n\text{–Mn–}(\mu_2\text{-COO})\text{–Mn–}(\mu_2\text{-COO})\text{–Mn–}(\mu_2\text{-COO})_n\text{–Mn–}$ (n = 4 and 2 for complex **1** and **2**, respectively), which are constructed alternatively from mononuclear [Mn^{II}] units and dinuclear $[Mn_2(FcCO_2)_4]$ units by μ_2-ferrocenecarboxylato-*O*,*O*′ bridging. The two Mn^{II} ions in the dinuclear $[Mn_2(FcCO_2)_4]$ units of complex **1** are connected by four ferrocenecarboxylato ligands to form a swastika-like shaped skeleton, which is rare in metallocenecarboxylato complexes. However, the two Mn^{II} ions in the dinuclear $[Mn_2(FcCO_2)_4]$ units of complex **2** are bridged only by two carboxylato ligands, and the other two ferrocenecarboxylato ligands in this unit bind in a chelating mode. The chains in complex **2** are further interconnected by the coordinated 4,4′-bipyridine molecules to form two-dimensional coordination sheets. Magnetic susceptibility measurements revealed a weak antiferromagnetic coupling for both complexes. A model Heisenberg chain comprising classical spins coupled through alternating exchange interactions J_1–J_1–J_2 (AF1–AF1–AF2) is proposed to describe the magnetic behavior.

Introduction

The chemistry of polynuclear manganese complexes has drawn significant research interest in the recent years due to their intriguing network topologies and their potential use as precursors for molecule-based magnetic materials.[1] To elucidate the fundamental relationship between the structures and the magnetic properties, a number of polynuclear manganese(II) complexes with various types of ligands have been synthesized and characterized in addition to the theoretical treatment provided in this paper.[2] Many factors govern the assembly process, and it is desirable to select the appropriate extended bridging ligands that can transmit magnetic interactions and bind several metal centers through various bonding modes and also to introduce some chelating or linear ditopic ancillary ligands to tune the composition and structure.[3,4] Carboxylato ligands have been widely used because they can exist in diverse coordination modes such 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.[5,6] However, most of the work has been focused on organic carboxylates such as oxalate, malonate, succinate, fumarate, maleate, terephthalate, 1,3,5-benzenetricarboxylate, and reports on organometallic carboxylates are limited. From the viewpoint of constructing functional manganese compounds, it may be interesting to incorporate the carboxyl group with the ferrocene moiety, for it was thought that, in addition to the electronic factors that are operative, the ferrocene moiety might introduce steric restrictions which might affect the nature of the adducts formed. Furthermore, the multicentered adducts may present opportunities for studying electronic interactions between the manganese center and the ferrocenyl groups. Ferrocenes not only show good redox activity but also play important roles in the field of materials science, as components of catalysts, molecular magnets, and nonlinear optical materials.[7] To the best of our knowledge, only three papers have been published on manganese complexes with ferrocene-involving carboxylate groups as ligands.[8–10] Among them, only the study reported by Hou, et al. includes some investigation of the magnetic properties of the manganese complex with a *p*-ferrocenylbenzoato ligand.[9] In the other two cases, Tian, et al.[8] and Kondo et al.[10] described the redox properties of a dinuclear complex cation $[Mn_2(phen)_4(FCA)_2]^{2+}$ (FCA = dianion of 3-ferrocenyl-2-crotonic acid, phen = 1,10-phenanthroline) and a manganese supercubane $[Mn_{13}O_8(OCH_3)_6(fcdc)_6]{\cdot}8H_2O{\cdot}2CH_3OH{\cdot}2(CH_3)_2CO$ (fcdc = 1, 1′-ferrocenedicarboxylato), respectively. This information led us to pursue the design and synthesis of manganese complexes with the participa-

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[a] College of Chemistry and Chemical Engineering, Guangxi Normal University,
Yucai Road 15, Guilin, 541004, China
Fax: +86-773-5832294
E-mail: fliangoffice@yahoo.com
[b] Department of Chemistry, College of Chemistry and Chemical Engineering and State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University,
Xiamen 361005, China

tion of ferrocene-involving carboxylato ligands and to investigate the magnetic properties of the compounds formed.

In this work, we chose ferrocenecarboxylato as the main ligand with the aim of investigating its ability to tune the structure and magnetic properties of Mn^{II} complexes. We present here the synthesis and characterization of two antiferromagnetic manganese coordination polymers, $[Mn_3(FcCO_2)_6(CH_3OH)_4]_n$ (**1**) and $[Mn_3(FcCO_2)_6(H_2O)_4(4,4'\text{-bpy})]_n$ (**2**). Both exhibit similar antiferromagnetic chains with a J_1–J_1–J_2 (AF1–AF1–AF2) repeating sequence, which is unprecedented in Mn^{II}–carboxylato complexes. The only reported Mn^{II}–carboxylato complexes with a J_1–J_1–J_2 repeating sequence exhibit ferrimagnetic properties with an AF–AF–F repeating sequence.[11]

Results and Discussion

Description of the Structure of Complexes 1 and 2

The X-ray diffraction analysis of complex **1** reveals an infinite 1D chain structure (Figure 1) with repeating linear trinuclear units $[Mn_3(FcCO_2)_6(CH_3OH)_4]$. It is shown in the structure that there are two kinds of coordination modes for the Mn^{II} ions. The $Mn2^{II}$ ion is six-coordinate in a distorted octahedral geometry and is coordinated by four oxygen atoms from four methanol molecules and two oxygen atoms from two ferrocenecarboxylato ligands (Figure 1). However, a distorted square-pyramidal coordination mode is established for the $Mn1^{II}$ ion, which is coordinated by five oxygen atoms from five ferrocenecarboxylato ligands. The Mn–O bond lengths of complex **1** are in the range 2.035(2)–2.227(3) Å (Table 1), which is comparable to those in related complexes.[3,12] The O–Mn–O angles range from 83.18 to 180.0° (Table 1). An interesting feature is the construction of the $[Mn_2(FcCO_2)_4]$ building block as shown in Figure 2. Two $Mn1^{II}$ ions are connected by four *syn-syn* μ_2-ferrocenecarboxylato ligands with a Mn···Mn separation of 3.0767(1) Å, and each ferrocenyl group points away from its neighbor. This gives a swastika-like shaped skeleton for the dimer structure when viewed down the Mn···Mn axis. To the best of our knowledge, only a few structures with Cu, Zn, Ru, and Mo were reported to have this kind of dimer skeleton with four μ_2-metallocenecarboxylato ligands.[13] This is the first report of such a structure for a Mn^{II}–metallocenecarboxylato complex. The short intradimer Mn···Mn separation is comparable to those reported for dinuclear Mn^{II} complexes bridged by four organic carboxylato ligands,[14] suggesting a nonbonding interaction between two Mn^{II} ions. Each $Mn1^{II}$ ion of the $[Mn_2(FcCO_2)_4]$ building block are connected to a $Mn2^{II}$ ion by one *syn-anti* ferrocenecarboxylato ligand with a Mn···Mn separation of 4.7884(3) Å, which is much larger than the intradimer Mn···Mn separation in the $[Mn_2(FcCO_2)_4]$ building block. A 1D infinite chain with repeating linear $[Mn_3(FcCO_2)_6(CH_3OH)_4]$ trinuclear units is thus formed along the *b* axis, in which both the $Mn2^{II}$ ion and the midpoint of the two $Mn1^{II}$ ions in the $[Mn_2(FcCO_2)_4]$ building block are located on the centers of symmetry. It is easy to see that all of the ferrocenecarboxylato ligands in the complex act as μ_2-bridges.

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

Mn2–O2	2.132(3)	Mn1–O4	2.108(3)
Mn2–O8	2.183(3)	Mn1–O5B	2.124(3)
Mn2–O7	2.227(3)	Mn1–O6	2.197(3)
Mn1–O3B	2.097(3)	Mn1–O1	2.035(2)
O2A–Mn2–O2	180.00(15)	O1–Mn1–O4	108.53(12)
O2–Mn2–O8A	91.44(13)	O3B–Mn1–O4	155.66(13)
O2–Mn2–O8	88.56(13)	O1–Mn1–O5B	112.47(11)
O8A–Mn2–O8	180.00(17)	O3B–Mn1–O5B	89.09(13)
O2–Mn2–O7A	92.33(11)	O4–Mn1–O5B	88.62(12)
O8–Mn2–O7A	91.75(11)	O1–Mn1–O6	91.56(10)
O2–Mn2–O7	87.67(11)	O3B–Mn1–O6	89.19(13)
O8–Mn2–O7	88.25(11)	O4–Mn1–O6	83.18(12)
O7A–Mn2–O7	180.0	O5B–Mn1–O6	155.96(11)
O1–Mn1–O3B	94.71(13)		

[a] Symmetry operations: (A) $-x + 2, -y + 1, -z$, (B) $-x + 2, -y + 2, -z$.

Complex **2** is different from complex **1**, and it displays a 2D layered structure parallel to the *ab* plane with the composition $[Mn_3(FcCO_2)_6(H_2O)_2(4,4'\text{-bpy})]_n$, as depicted in Figure 3. The coordination modes of the Mn^{II} ions in complex **2** (Figure 4) are similar to those in complex **1**. The $Mn2^{II}$ ion is coordinated in a distorted octahedral geometry by two oxygen atoms from water molecules, two nitrogen atoms from two 4,4′-bpy ligands, and two oxygen atoms from two ferrocenecarboxylato ligands. The $Mn1^{II}$ ion is in a distorted square-pyramidal environment and is coordinated by five oxygen atoms from four ferrocenecarboxylato ligands. Thus, there are two kinds of coordination modes (chelating and *syn-anti* μ_2-bridging) for the ferrocenecarboxylato ligands in complex **2**. The Mn–O bond lengths are in the range 2.056(5)–2.257(5) Å, and the O–Mn–O bond angles vary from 58.50(19) to 180.0° (Table 2). Two $Mn1^{II}$ ions of complex **2** are bridged by two *syn-anti* μ_2-ferrocenecarboxylato ligands to form a dimer building block $[Mn_2(FcCO_2)_4]$ with a Mn···Mn separation of 3.7757(2) Å, which is shorter than those for the reported dimers with two μ_2-carboxylato-*O*,*O′* ligands.[15–17] It is noteworthy that

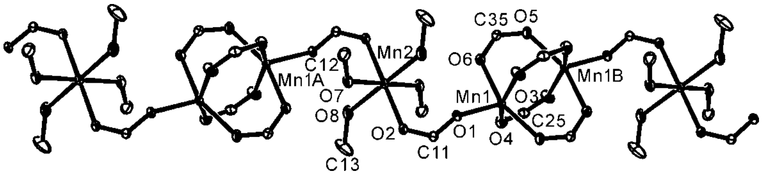
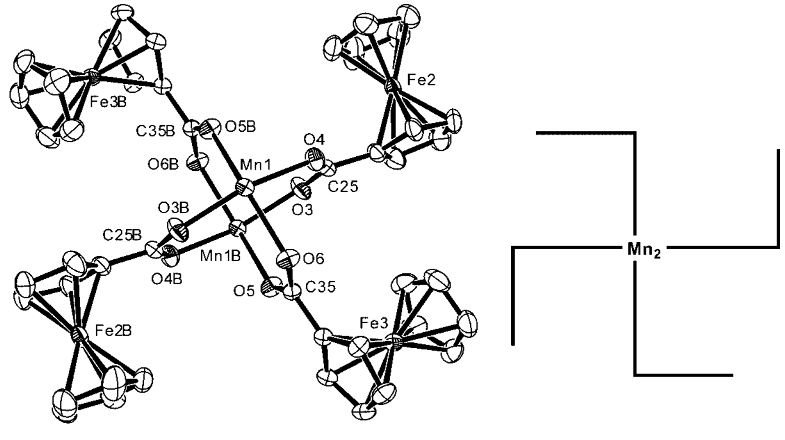


Figure 1. 1D infinite chain of complex **1** showing 30% probability ellipsoids. For clarity, ferrocenyl groups and hydrogen atoms are omitted. Symmetry operations: (A) $-x + 2, -y + 1, -z$, (B) $-x + 2, -y + 2, -z$.



(a) (b)

Figure 2. (a) The $[Mn_2(FcCO_2)_4]$ building block of complex **1**. Symmetry operations: (B) $-x + 2$, $-y + 2$, $-z$. (b) The skeletal swastika-like shape of $[Mn_2(FcCO_2)_4]$ of complex **1** when viewed down the Mn···Mn axis.

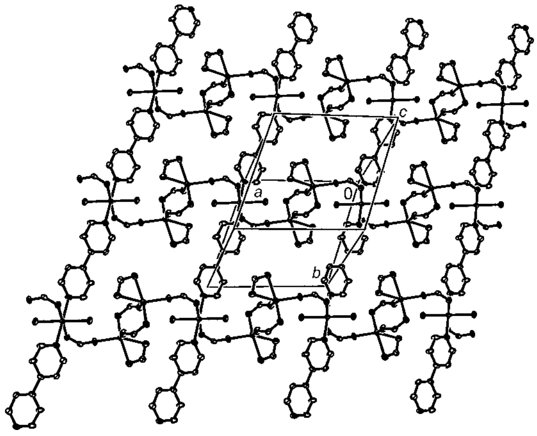


Figure 3. 2D network of complex **2**. Ferrocenyl groups and hydrogen atoms are omitted for clarity.

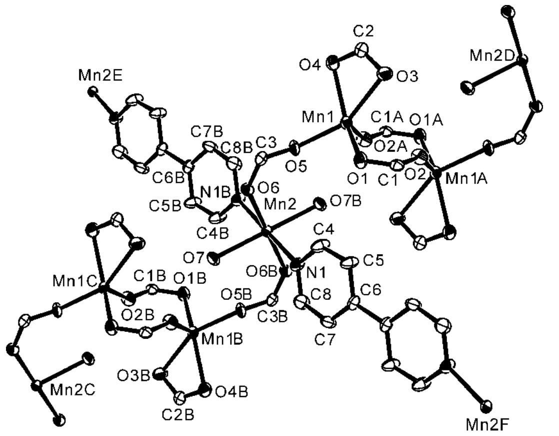


Figure 4. ORTEP drawing of complex **2** showing 30% probability ellipsoids. For clarity, ferrocenyl groups and hydrogen atoms are omitted and only selected atoms are labeled. Symmetry operations: (A) $-1 - x$, $1 - y$, $1 - z$, (B) $-x$, $1 - y$, $1 - z$, (C) $1 + x$, y, z, (D) $-1 + x$, y, z, (E) x, $1 + y$, z, (F) x, $-1 + y$, z.

the dimer building blocks in complex **1** and **2** have the same composition but different structures. All of the ferrocenecarboxylato ligands in the dimer of complex **1** behave as *syn-syn* μ_2-bridging ligands to bridge the two Mn^{II} ions. However, only two ferrocenecarboxylato ligands in the dimer of **2** act as *syn-anti* μ_2-bridging ligands, the other two chelate to Mn^{II} ions. This results in a much shorter Mn···Mn separation for complex **1** than that for complex **2**. Each $Mn1^{II}$ ion of the dimer building block in complex **2** is further connected to one $Mn2^{II}$ ion by one *syn-anti* μ_2-ferrocenecarboxylato bridge with a Mn···Mn separation of 5.1268(3) Å. This leads to the formation of an infinite 1D chain along the *a* axis, which has linear trimer repeating units of $[Mn_3(FcCO_2)_6(H_2O)_2]$. The 1D chains are further connected by the coordination of 4,4′-bpy molecules to $Mn2^{II}$ ions from adjacent chains with an interchain Mn···Mn separation of 11.493 Å, resulting in the construction of a 2D coordination sheet in the *ab* plane, as shown in Figure 3. The two pyridine rings of the 4,4′-bpy molecule are parallel to each other. In the structure of complex **2**, both the $Mn2^{II}$ ion and the midpoint of two $Mn1^{II}$ ions in the dimer are located on the centers of symmetry.

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

Mn1–O2A	2.056(5)	Mn1–O3	2.275(5)
Mn1–O5	2.070(5)	Mn2–O6	2.166(4)
Mn1–O1	2.128(5)	Mn2–O7	2.195(5)
Mn1–O4	2.179(5)	Mn2–N1	2.257(5)
O2A–Mn1–O5	87.61(19)	O6B–Mn2–O7B	84.23(18)
O2A–Mn1–O1	116.9(2)	O6–Mn2–O6B	180.00(9)
O5–Mn1–O1	96.7(2)	O6–Mn2–O7B	95.77(18)
O2A–Mn1–O4	100.8(2)	O6–Mn2–O7	84.23(18)
O5–Mn1–O4	100.4(2)	O7B–Mn2–O7	180.0
O1–Mn1–O4	139.1(2)	O6–Mn2–N1	91.5(2)
O2A–Mn1–O3	110.3(2)	O7–Mn2–N1	92.8(2)
O5–Mn1–O3	153.8(2)	O6–Mn2–N1B	88.5(2)
O1–Mn1–O3	92.1(2)	O7–Mn2–N1B	87.2(2)
O4–Mn1–O3	58.50(19)	N1–Mn2–N1B	180.0(3)

[a] Symmetry operations: (A) $-x - 1$, $-y + 1$, $-z + 1$, (B) $-x$, $-y + 1$, $-z + 1$.

It is of great interest that both compounds have similar chains constructed from alternately repeating mononuclear [Mn^{II}] units and dinuclear [$Mn_2(FcCO_2)_4$] units. The big difference is that the two Mn^{II} ions in the dinuclear [$Mn_2(FcCO_2)_4$] units of compound **2** are bridged only by two *syn-anti* carboxylato ligands; the other two carboxylato ligands in this unit act as chelating ligands. However, the two Mn^{II} ions in the dinuclear [$Mn_2(FcCO_2)_4$] units of compound **1** are connected by four *syn-syn* carboxylato ligands, that is to say, all of the ferrocenecarboxylato ligands in the dinuclear unit of compound **1** behave as μ_2-bridging ligands. Another difference is that the chains in compound **2** are further interconnected by the coordinated 4,4′-bipyridine molecules to form two-dimensional coordination sheets.

Magnetic Properties

The magnetic properties of complexes **1** and **2** were investigated by solid-state magnetic susceptibility (χ_m) measurements in the 2.0–300 K range in a DC field of 2000 Oe; the resulting data are shown in Figure 5 and Figure 6 as χ_m and $\chi_m T$ vs. T plots. The χ_m value decreases monotonously with T for both compounds. Its values at 300 K and 2 K are 0.03274 and 1.8322 cm^{3}mol^{-1}, respectively, for compound **1**, and 0.04101 and 1.331 cm^{3}mol^{-1}, respectively, for compound **2**. The values of $\chi_m T$ at 300 K for compounds **1** and **2** are 9.82 and 12.30 cm^{3}mol^{-1} K, respectively, which are lower than that (13.1 cm^{3}mol^{-1}K) expected for three magnetically isolated high-spin Mn^{II} ions. This indicates the presence of antiferromagnetic coupling. With decreasing temperature, the $\chi_m T$ of **1** and **2** gradually decrease, reaching 3.66 and 2.66 cm^{3}mol^{-1}K, respectively, at 2.0 K. The shapes of these curves are also characteristic of weak antiferromagnetic interactions between the Mn^{II} centers.

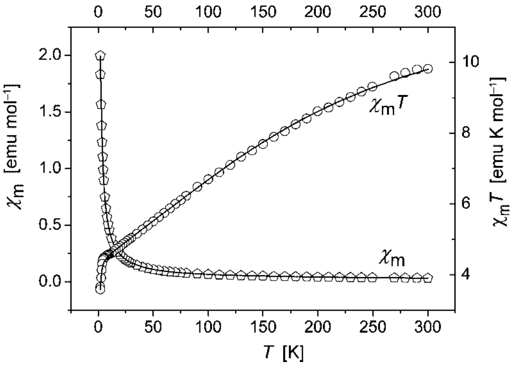


Figure 5. Plot of χ_m and $\chi_m T$ vs. T for **1**. Solid lines show the best fit of the data according to the proposed model.

There are two sets of magnetic exchange pathways within the chain in both compounds. One consists of one *syn-anti* μ_2-1,3-carboxylato bridge. The other mainly consists of four *syn-syn* μ_2-1,3-carboxylato bridges for compound **1** and two *syn-anti* μ_2-1,3-carboxylato bridges for compound **2**. The interactions alternate according to a J_1–J_1–J_2 repeating sequence to yield an antiferromagnetic chain (AF1–AF1–AF2) as shown in Scheme 1. This unprecedented antiferromagnetic chain is different from the reported AF–AF–F ferrimagnetic chains.[11,18] The ground state is S = 5/2 for each trinuclear Mn_3 unit.

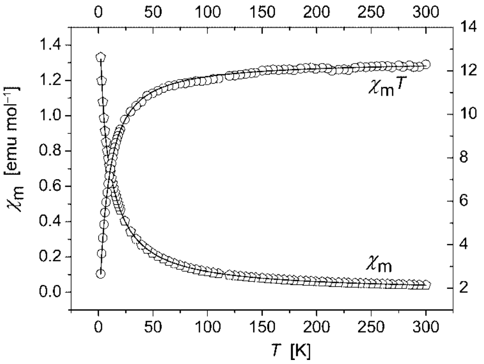
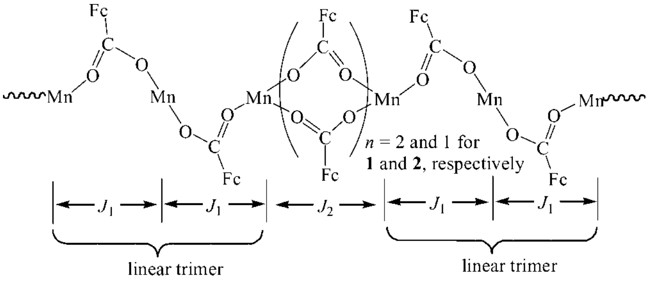


Figure 6. Plot of χ_m and $\chi_m T$ vs. T for **2**. Solid lines show the best fit of the data according to the proposed model.



Scheme 1.

The theoretical expression proposed by Escuer and Ribas et al.[11,18] was employed to fit the observed magnetic data for complexes **1** and **2**:

$H = -J_1\Sigma(S_{3i}\cdot S_{3i+1} + S_{3i+1}\cdot S_{3i+2}) - J_2\Sigma S_{3i-1}\cdot S_{3i}$

$$\chi_{chain} = \frac{Ng^2\mu_B^2}{3kT}\frac{3(1-\mu_1^4\mu_2^2)+4\mu_1(1-\mu_1^2\mu_2^2)+2\mu_2(1+\mu_1)^2(1-\mu_1^2)+2\mu_1^2(1-\mu_2^2)}{(1-\mu_1^2\mu_2)^2}$$

where $\mu_1 = \coth(J_1/kT) - kT/J_1$, $\mu_2 = \coth(J_2/kT) - kT/J_2$, $J_i = J_iS(S + 1)$ and $g_i = g_i[S(S + 1)]^{1/2}$. The best fitting parameters obtained for **1** are J_1 = –0.15 cm^{-1}, J_2 = –29.56 cm^{-1}, and g = 2.00 with $R = 3.73\times10^{-4}$.

For complex **2**, the fitting was carried out by employing a molecular field approximation, assuming that there is an interchain interaction (zJ') through the 4,4′-bpy bridge. With this assumption, the final susceptibilities for **2** are shown below:

$$\chi_M = \frac{\chi_{chain}}{1-(zJ'/Ng^2\beta^2)\chi_{chain}}$$

The best fitting parameters for **2** were found to be J_1 = –0.27 cm^{-1}, J_2 = –1.28 cm^{-1}, zJ' = –0.081 cm^{-1}, g = 1.95 with $R = 1.32\times10^{-5}$. This fit gives a nice agreement factor R. It was revealed that the 4,4′-bpy ligand (between the chains) mediates a very weak antiferromagnetic interaction (zJ' = –0.081 cm^{-1}), in agreement with the large Mn···Mn separation (11.493 Å).

These *J* values are comparable to those of compounds with similar bridging modes and also confirm the dependence of *J* on the nature of the carboxylato bridges.[19,20] The adjacent trinuclear units of **1** are bridged by four *syn-syn* μ_2-1,3-carboxylato ligands which are much more efficient pathways for superexchange than *syn-anti* μ_2-1,3-carboxylato bridges. Thus, they induce a much larger $|J|$ (J_2 = –29.56 cm^{-1}) than that (J_1 = –0.15 cm^{-1}) in the trimer of **1** and those (J_1 = –0.27 cm^{-1}, J_2 = –1.28 cm^{-1}) in **2**. The intratrimer *J* (J_1 = –0.27 cm^{-1}) and intertrimer *J* (J_2 = –1.28 cm^{-1}) of **2** are in the range reported for one *syn-anti* carboxylato bridge (–0.1 to –0.4 cm^{-1})[5,17,21] and two *syn-anti* carboxylato bridges (–0.9 to –1.7 cm^{-1}),[16,17,20] respectively. This confirms again that the magnitude of $|J|$ increases with the number of carboxylato bridges.

Conclusions

Two manganese(II) complexes bearing the organometallic ligand ferrocenecarboxylato have been synthesized and characterized crystallographically and magnetically. Both complexes have similar chains constructed by μ_2-ferrocenecarboxylato-*O,O′* bridging from alternately repeating mononuclear [Mn^{II}] units and dinuclear [$Mn_2(FcCO_2)_4$] units. The dinuclear [$Mn_2(FcCO_2)_4$] unit of complex **1** presents a swastika-like shaped skeleton, which is rare in metallocenecarboxylato complexes. Both compounds show antiferromagnetic interactions with a J_1–J_1–J_2 repeating sequence. To the best of our knowledge, this is the first AF1–AF1–AF2 antiferromagnetic chain with an organometallic carboxylato bridge. The analysis of the magnetic properties also confirms that the exchange coupling through the carboxylato bridge is highly dependent on the conformation modes of the bridge between the metal atoms. The *syn-syn* mode usually induces a much larger $|J|$ value than the *syn-anti* mode, and the magnitude of $|J|$ increases with the number of carboxylato bridges.

Experimental Section

General: Sodium ferrocenecarboxylate was prepared according to the literature method.[22] The other starting materials were commercially available and were used without further purification. Elemental analyses (C, H, and N) were performed with a Vario EL analyzer. Infrared spectra were recorded with KBr pellets by using a Nicolet 360 FT-IR spectrometer in the region 400–4000 cm^{-1}. Variable-temperature magnetic susceptibility data were obtained with a SQUID magnetometer (MPMS XL-5) in the temperature range 2–300 K with an applied magnetic field of 2000 Oe.

CAUTION: Although no problems were encountered in this work, perchlorate salts are potentially explosive. They should be prepared in small quantities and handled with great care.

Preparation of [$Mn_3(FcCO_2)_6(CH_3OH)_4$]$_n$ (1): A methanol solution (5 mL) of $FcCO_2Na$ (0.0251 g; 0.1 mmol) was added dropwise to a methanol solution (5 mL) of $Mn(ClO_4)_2·6H_2O$ (0.0362 g; 0.1 mmol). The resulting mixture was stirred at room temperature for 10 h and filtered. The filtrate was allowed to condense at ambient temperature to give orange crystals. Yield: 0.0584 g (70%). $C_{70}H_{70}Fe_6Mn_3O_{16}$ (1667.18): calcd. C 50.38, H 4.20; found C 50.67, H 4.24. IR (KBr): ṽ = 3431 (m), 1533 (s), 1391 (s), 1360 (s), 1105 (w), 1001 (w), 816 (m), 506 (m), 486 (m) cm^{-1}.

Preparation of [$Mn_3(FcCO_2)_6(H_2O)_2$(4,4′-bpy)]$_n$ (2): A methanol solution (5 mL) of $FcCO_2Na$ (0.0251 g; 0.1 mmol) was added dropwise to a methanol solution (10 mL) of 4,4′-bpy (0.0156 g, 0.1 mmol) and $Mn(ClO_4)_2·6H_2O$ (0.0362 g; 0.1 mmol). The resulting solution was stirred at ambient temperature for 10 h and filtered. The filtrate was allowed to condense at ambient temperature to give orange crystals. Yield: 0.0519 g (60%). $C_{76}H_{66}Fe_6Mn_3N_2O_{14}$ (1731.23): calcd. C 52.68, H 3.81, N 1.61; found C 53.01, H 3.97, N 1.47. IR (KBr): ṽ = 3431 (m), 1607 (w), 1577 (s), 1531 (s), 1391 (s), 1359 (s), 1218 (w), 1105 (w), 1002 (w), 811 (m), 508 (m), 487 (w) cm^{-1}.

X-ray Crystallography: All the data for complexes **1** and **2** were collected with a Bruker APEX CCD diffractometer by using graphite monochromatic Mo-K_α radiation (λ = 0.71073 Å). A prismatic single crystal was mounted on a glass fiber. The data were collected at 296(2) K. Absorption effects were corrected by semi-empirical methods. The structure was solved by direct methods with the program SHELXS-97[23] and refined by full-matrix least-squares methods on all F^2 data with SHELXL-97.[24] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules and hydroxyl groups were located in a difference Fourier map and refined isotropically in the final refinement cycles. Other hydrogen atoms were placed in calculated positions and refined by using a riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. The molecular illustrations were drawn with the program XP.[25] All cal-

Table 3. Crystal data and refinement details of complexes **1** and **2**.

	1	**2**
Formula	$C_{70}H_{70}Fe_6Mn_3O_{16}$	$C_{76}H_{66}Fe_6Mn_3N_2O_{14}$
M [g mol^{-1}]	1667.18	1731.23
T [K]	296(2)	296(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.9256(7)	10.9802(7)
b [Å]	12.0542(7)	11.4929(7)
c [Å]	13.0976(8)	14.8800(9)
α [°]	88.4100(10)	82.3570(10)
β [°]	78.9410(10)	83.4290(10)
γ [°]	63.5120(10)	65.9560(10)
V [Å^3]	1650.30(17)	1695.84(18)
Z	1	1
$D_{calcd.}$ [g cm^{-3}]	1.678	1.695
μ, Mo-K_α [mm^{-1}]	1.901	1.852
F(000)	849	879
Crystal size [mm]	0.27 × 0.11 × 0.08	0.25 × 0.15 × 0.05
θ range for data	1.59–25.90°	1.38–25.01°
Reflections collected	9069	10094
Unique reflections (R_{int})	6284 (0.0597)	5917 (0.0548)
Completeness to θ_{max}	98.0%	98.9%
Max. and min. transmission	0.8628 and 0.6279	0.9131 and 0.6546
Data/restraints/parameters	6284–2–431	5917–3–463
Goodness of fit on F^2	0.993	1.279
Final *R* indices[a] [$I > 2\sigma(I)$]	R_1 = 0.0531	R_1 = 0.0863
Final wR_2 indices[a]	wR_2 = 0.1352	wR_2 = 0.1522
Final *R* (for all data)[a]	R_1 = 0.0639,	R_1 = 0.0982
Final wR_2 (for all data)[a]	wR_2 = 0.1421	wR_2 = 0.1575
Largest diff. peak and hole [e Å^{-3}]	0.858 and –0.933	0.724 and –0.624

[a] $R_1(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

culations were performed with the WinGX System 1.64.05.[26] Crystallographic data for compounds **1** and **2** are given in Table 3. Selected bond lengths and bond angles are given in Table 1 and Table 2.

CCDC-621075 and CCDC-621076 (for complexes **1** and **2**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

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