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Synthesis, Structure, and Magnetism of a 1D Compound Engineered from a Biradical [5,5′-Bis(3′′-oxide-1′′-oxyl-4′′,4′′,5′′,5′′-tetramethylimidazolin-2′′-yl)-2,2′-bipyridine] and $Mn^{II}(hfac)_2$

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The synthesis, crystal structure, and magnetic properties of a one-dimensional compound, $\{[Mn(hfac)_2]_2(biradical)\}_n$ **(1),** resulting from the coordination of bis(hexafluoroacethylacetonato)manganese(II) $[Mn(hfac)_2]$ with a biradical obtained by grafting two nitronyl nitroxide radicals in the 5 and 5′ positions of a 2,2′-bipyridine ligand are described. Compound **1** crystallizes in the triclinic $P\bar{1}$ space group with the following parameters: $a = 11.905(2)$ Å, $b = 12.911(2)$ Å, $c = 20.163(3)$ Å, $\alpha = 73.556(3)°$, $\beta = 80.850(3)°$, $\gamma = 82.126(3)°$, $Z = 2$. The bipyridyl moiety acts as a chelate toward one $[Mn(hfac)_2]$ unit, while the pendent nitronyl nitroxide radicals are symmetrically bound in *trans*-configuration to additional $[Mn(hfac)_2]$ units. The result is infinite chains running along the *c* axis direction with the biradical bridging $[Mn(hfac)_2]$ units with pending bipyridine/$Mn(hfac)_2$ cores. The magnetic behavior is characteristic of ferrimagnetic chains. Qualitatively we observe first the antiferromagnetic coupling (J_2) of each manganese(II) center with two nitronyl nitroxide moieties, leading to a minimum in the χT product of 6.63 emu K mol^{-1} observed at 70 K and corresponding to a ground spin state $S = 3/2$ plus one extra spin $S = 5/2$ coming from the pending manganese(II) center. The increase of χT at lower temperature is understood as a fictive ferromagnetic coupling related to the true antiferromagnetic coupling J_1 of the pseudospin $S = 3/2$ with spin $S = 5/2$ of the pending manganese(II). Along this approach ($H = -JS_iS_j$) the best fit (300–8 K) of the experimental data leads to $J_1 = -0.622 \pm 0.022$ cm^{-1} and $J_2 = -203 \pm 3$ cm^{-1} with g(Rad) $= 2.0017 \pm 0.0015$ and g(Mn) $= 2.0017 \pm 0.0015$.

In the field of molecule-based magnetic materials the engineering approach based on metal coordination of nitroxide free radicals has been the subject of numerous reports since it was discovered more than a decade ago.[1,2] This could be ascribed to the versatility of the magnetic compounds which can be obtained by coordination of magnetogen metal centers with such stable organic spin carriers. Indeed, on one hand by means of coordination chemistry it is today possible to build with a great predictability numerous metal coordination networks exhibiting various topologies, dimensionalities, and properties. On the other hand, nitroxide radicals are easy to produce in a great variety of forms to fit almost any particular organic fragment and have proved to be very stable even in the presence of metal ions. Therefore, whereas the metal—radical approach is not restricted to nitroxide free radicals, they have gained predominance in the formation of metal-induced self-organized molecular structures with magnetic properties. The main limitation is the low Lewis

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basicity of the nitroxyl group (N−O), resulting in a poor ability to coordinate. However, this is generally easily overcome, by using acidic metal centers, such as the hexafluoroacetylacetonatometal[3−5] or the trifluoroacetatometal[6] complex precursors. An alternative way, which we have helped to develop, is to incorporate the N−O group in a chelate ring to force the metal to coordinate.[7] This way has proved to be particularly productive, allowing the coordination of most metal ions without the requirement of bulky and electron-withdrawing ancillary ligands. Along the chelating approach most results were obtained with nitronyl or imino nitroxide radicals grafted onto pyridine,[8−11] imidazole,[12−14] benzimidazole,[15−17] bipyridine,[18−21] terpyridine,[22] phenanthroline,[23] and triazole scaffolds.[24−26]

In this Article we report a 1D chain compound generated from biradical **L** (Figure 1) which was obtained by connecting two nitronyl nitroxide radicals in the 5 and 5′ substitution positions of a 2,2′-bipyridine core. In contrast with our previous works with biradicals based on oligopyridine,[18−21] the nitronyl nitroxide radicals are not connected in the ortho position of the nitrogen atoms, excluding any chelating effect toward the nitroxyl groups. This was intentionally done with the idea that the nitronyl nitroxide radical moieties would allow the building of metal−radical chains after reaction with hexafluoroacethylacetonatometal complexes as demonstrated in early reports,[1,2,27−30] and then to assemble these chains in 3D networks by connecting them through the coordination of the bipyridyl moieties with a second metal ion. In this Article we report the result obtained by reacting bis(hexafluoroacethylacetonato)manganese(II) with biradical **L** (Figure 1).

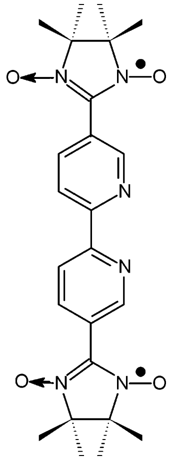

Figure 1. Chemical structure of the biradical **L**.

Experimental Section

$\{[Mn(hfac)_2]_2(biradical)\}_n$ (1). $Mn(hfac)_2.2H_2O$ (141 mg, 0.3 mmol) was dissolved in 10 mL of boiling heptane to azeotropically remove hydration water molecules. After complete dissolution a few drops of dichloromethane were added to avoid crystallization upon cooling. The solution was then deposited in a test tube on the top of a 10 mL dichloromethane solution of the biradical (44 mg, 0.1 mmol). Small dark crystals (0.1 × 0.1 × 0.1 mm) were obtained after 10 days of interdiffusion of the two solutions. Anal. Calcd for $Mn_2C_{44}H_{34}F_{24}N_6O_{12}$: Mn, 7.82; C, 37.62; H, 2.43; F, 32.46; N, 5.98; O, 13.67. Found: Mn, 7.90; C, 37.48; H, 2.65; F, 33.04; N, 5.90.

Crystallography. Data were collected at room temperature (300 K) with a Bruker SMART CCD diffractometer equipped with a normal focus molybdenum-target X-ray tube ($\lambda = 0.71073$ Å). The data were processed through the SAINT[31] data reduction and absorption correction software to give 19204 collected reflections from which 13480 [$R_{int} = 0.0984$] were independent. The structures were solved and refined by the full-matrix least-squares method on F^2 using the SHELXTL[32] software. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated positions with isotropic thermal parameters. Detailed crystallographic data are gathered in Table 1.

Magnetic Susceptibility Measurements. The magnetic susceptibilities were measured on the polycrystalline sample in the range 2−300 with a Quantum Design MPMS SQUID magnetometer operating at a field strength of 0.5 T. The data were corrected for diamagnetism of the constituent atoms using Pascal constants.

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Table 1. Crystal Data and Structure Refinement Parameters for **1**

empirical formula	$C_{44}H_{34}F_{24}Mn_2N_6O_{12}$
fw	1404.65
T (K)	298(2)
space group	$P\bar{1}$
a (Å)	11.9054(17)
b (Å)	12.9108(19)
c (Å)	20.163(3)
α (deg)	73.556(3)
β (deg)	80.850(3)
γ (deg)	82.126(3)
V (Å^3)	2920.8(7)
Z	2
μ(Mo Kα) (mm^{-1})	0.569
d_{calcd} (cm^3)	1.597
λ (Å)	0.71073
$R(F)$,^{a} $I > 4\sigma(F_o)$	0.0970
$R_w(F^2)^a$	0.2864

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w(F^2) = \Sigma[w((F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**

Mn1	O7	2.106(4)	Mn2	O11	2.137(4)
Mn1	O5	2.139(5)	Mn2	O1	2.138(4)
Mn1	O6	2.150(4)	Mn2	O12	2.159(5)
Mn1	O8	2.153(4)	Mn3	O9	2.141(4)
Mn1	N5	2.273(4)	Mn3	O3	2.149(4)
Mn1	N6	2.278(4)	Mn3	O10	2.169(4)
O1	N1	1.287(6)	O2	N2	1.248(6)
O3	N3	1.294(5)	O4	N4	1.280(6)

O7	Mn1	O5	87.51(17)	O6	Mn1	N5	92.85(16)
O7	Mn1	O6	99.43(16)	O8	Mn1	N5	103.60(16)
O5	Mn1	O6	82.46(17)	O7	Mn1	N6	95.61(16)
O7	Mn1	O8	83.40(16)	O5	Mn1	N6	105.17(17)
O5	Mn1	O8	161.52(15)	O6	Mn1	N6	163.45(16)
O6	Mn1	O8	83.21(17)	O8	Mn1	N6	91.74(17)
O7	Mn1	N5	166.56(16)	N5	Mn1	N6	72.96(16)
O5	Mn1	N5	88.71(17)				
O11	Mn2	O1#1	84.14(15)	O9	Mn3	O3#2	86.36(15)
O11	Mn2	O1	95.86(15)	O9	Mn3	O3	93.64(15)
O11#1	Mn2	O12	97.02(17)	O9	Mn3	O10	82.35(15)
O11	Mn2	O12	82.98(17)	O3	Mn3	O10	96.26(15)
O1	Mn2	O12	94.61(17)	O9	Mn3	O10#2	97.65(15)
O1	Mn2	O12#1	85.39(17)	O3	Mn3	O10#2	83.74(15)
N1	O1	Mn2	134.3(4)	N3	O3	Mn3	129.3(3)

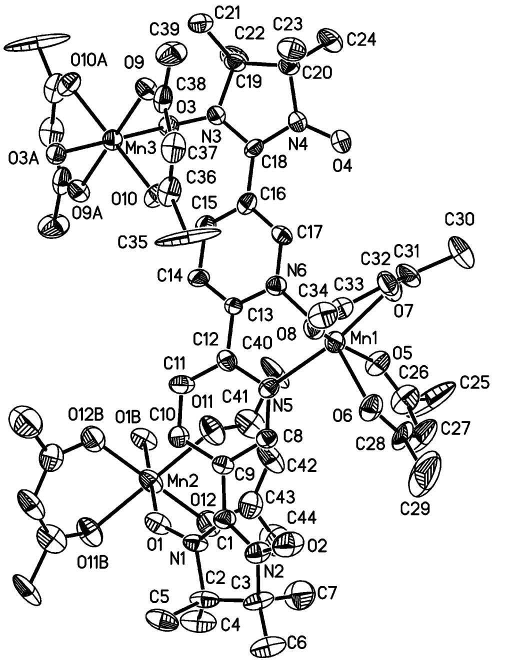

Figure 2. Molecular building block $\{[Mn(hfac)_2]_2(biradical)\}$. The fluorine atoms are omitted for clarity.

Results and Discussion

Crystal Structure. A view of the asymmetric unit with labeled atoms is shown in Figure 2, and a selection of interatomic distances and angles is given in Table 2. Compound **1** was obtained by reacting bis(hexafluoroacetylacetonato)manganese(II) $[Mn(hfac)_2]$ with bisradical **L** (Figure 1) and crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit comprises one ligand, one $[Mn(hfac)_2]$ (Mn1), and two half-$[Mn(hfac)_2]$ (Mn2, Mn3) units. The nitrogen atoms (N5, N6) of the bipyridyl moiety of the ligand act as a chelate toward Mn1 [Mn1−N5 = 2.273(4) Å and Mn1−N6 = 2.278(4) Å] with a bite angle of 73.0(2)° for (N5−Mn−N6). Both nitronyl nitroxide radical moieties are bound in *trans*-configuration to a $[Mn(hfac)_2]$ unit by one of their oxygen atoms, O1 and O3, respectively, to Mn2 and Mn3 [Mn2−O1 = 2.138(4) Å and Mn3−O3 = 2.149(4) Å]. The two manganese(II) ions, Mn2 and Mn3, are located on inversion centers, respectively (0,0,0) and (0,0,0.5).

As a result this compound forms infinite chains parallel to the c axis direction along which the biradical **L** bridges the manganese(II) ions Mn2 and Mn3 with the pending manganese(II) ion Mn1 in between (Figure 3). The coordination geometries around Mn2 and Mn3 show only small differences. The Mn−O(hfac) bond lengths are close [2.137(4) and 2.159(4) Å for Mn2 and 2.141(4) and 2.169(4) Å for Mn3]. A more significant difference is found in the N−O−Mn angles [N1−O1−Mn2 = 134.3(4)° and N3−O3−Mn3 = 129.3(3)°]. No significant contacts were found between the chains.

Magnetic Properties. At 300 K the product (χT) of the molar magnetic susceptibility (χ) with temperature (T) is 7.13 emu K mol^{-1}, which is less than the value ($\chi T = 9.50$ cm^3 K mol^{-1}) expected if the two manganese(II) ions with spin $S = 5/2$ and the bisradical molecule with two spins $S = 1/2$ of the molecular unit $\{[Mn(hfac)_2]_2(biradical)\}$ were magnetically independent. Upon cooling, χT decreases first, reaches a rounded minimum at 70 K (6.61 emu K mol^{-1}), and then increases at lower temperature (Figure 4). At 2 K the magnetization increases continuously as the magnetic field increases, but it does not reach saturation at $H = 55000$ G (Figure 5). Further measurement at low temperature (0.5−5 K) of the alternating current susceptibility and direct current magnetization did not reveal any 3D long-range magnetic order.

In compound **1** we may consider at least three magnetic interactions within the chain (Figure 3). One magnetic interaction (J_1) results from the coupling of Mn1 manganese(II) ions with the nitronyl nitroxide radicals through the bipyridyl moiety. Two other magnetic interactions (J_2 and J_3) couple each nitronyl nitroxide radical with, respectively, the Mn2 and Mn3 manganese(II) ions (Figure 3). Owing to the structural features and previous publications on magnetic interaction between Mn^{II} and nitroxide radicals,[2] the interactions J_2 and J_3 are expected to be equal, antiferromagnetic, and predominant ($\sim\angle 200$ cm^{-1}). The interaction J_1 between the radical and Mn1 through the bipyridyl nitrogen atoms

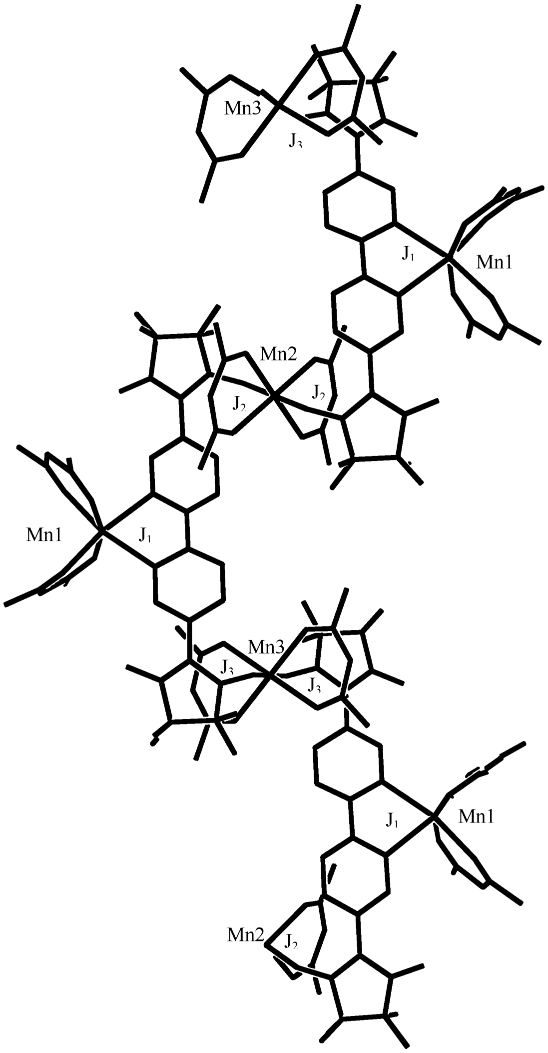

Figure 3. Drawing showing a chain of compound **1** developing along the *c* axis. J_1, J_2, and J_3 hold for the predominant Mn−radical magnetic interactions.

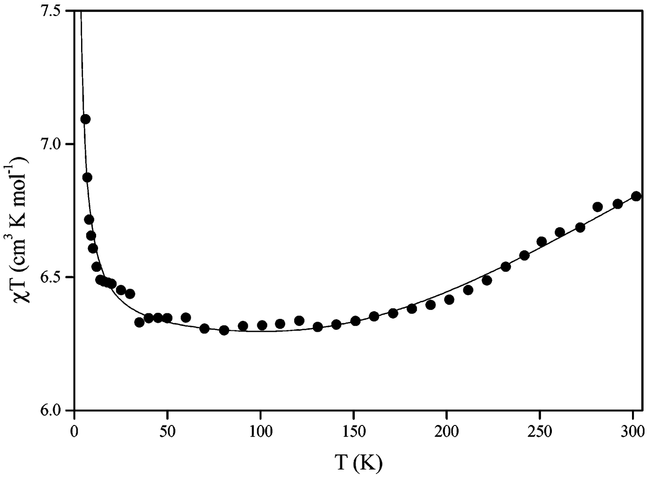

Figure 4. Temperature dependence of the product of the molar magnetic susceptibility χ with temperature (χT) for compound **1** as black circles. The solid line holds for the best fit of the data with values in the text.

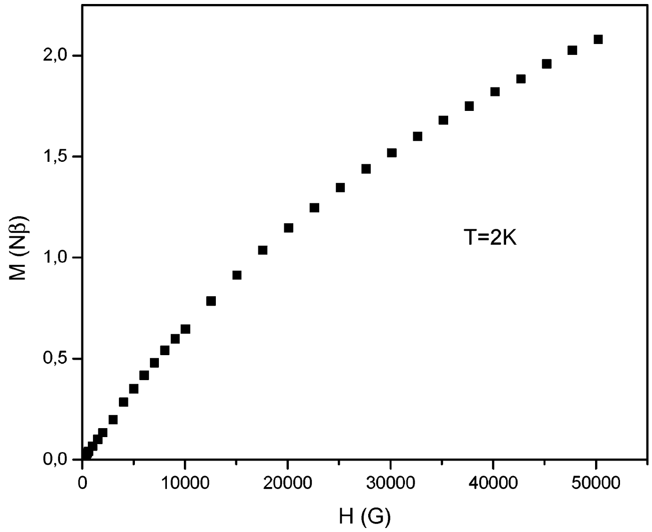

Figure 5. Magnetic field dependence of the magnetization at 2 K for compound **1**.

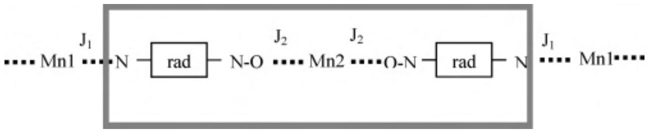

Figure 6. Schematic representation of the model used for the fitting of the temperature dependence of the magnetic susceptibility. Inside the gray frame is the Rad−Mn^{II}−Rad system treated as an effective spin coupled ferromagnetically with spin $S = 5/2$ of manganese(II) Mn1.

should be antiferromagnetic but weak ($|J_1| < 14$ cm^{-1}).[33] We may also consider an additional magnetic interaction coupling the radicals through the bipyridyl moiety, but measurement of the magnetic susceptibility carried out on frozen solutions of the free radical showed it to be negligible. Therefore, the interpretation of the magnetic behavior is similar to a ferrimagnetic chain in which alternated spins $S = 1/2$ and $S = 5/2$ are antiferromagnetically coupled but with different values of the exchange coupling.

Qualitatively we observe first the coupling of the manganese(II) ions Mn2 and Mn3 with the two nitronyl nitroxide moieties, and the minimum of 6.63 emu K mol^{-1} observed at 70 K is indeed close to the value expected for a ground spin state $S = 3/2$ plus one spin $S = 5/2$ coming from Mn1 (6.25 emu K mol^{-1}, $g = 2$). The increase at lower temperature can be view then as a fictive ferromagnetic coupling of the pseudospin $S = 3/2$ with spin $S = 5/2$ of Mn1.

Therefore, the experimental data have been fitted by an approach that relates quantum and classical spins. For simplicity in the model proposed for **1**, J_2 and J_3 (Figure 3) have been considered as equal as shown in Figure 6. First, the Rad−Mn^{II}−Rad unit (where Rad is the radical) has been exactly solved using quantum spins. At this point, three approaches can be used to describe the magnetic behavior of **1** at low temperature.

(1) Only the ground spin state ($S = 3/2$) of the Rad−Mn^{II}−Rad unit is populated at low temperature. In this way, our chain can be described as a 3/2−5/2 regular chain with an effective exchange ferromagnetic coupling related to the true antiferromagnetic coupling through the effective and true spin moments and the radical spin densities.

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(2) All spin states of the Rad$-$Mn$^{II}-$Rad unit (3/2, 5/2, 5/2, 7/2) can be populated at low temperature. So our system could be described by four regular chains corresponding to the mentioned four spin states. These chains show different effective magnetic couplings related to the true magnetic coupling in a known way. The contribution of each one of these one-dimensional behaviors is ruled by the thermal Boltzmann distribution.

(3) All spin states of the Rad$-$Mn$^{II}-$Rad unit (3/2, 5/2, 5/2, 7/2) can be populated at low temperature. So our one-dimensional system can also be described as the only regular chain. In this case, only one effective exchange magnetic coupling and one effective spin for the Rad$-$Mn$^{II}-$Rad unit are considered. These effective values are obtained from the thermal Boltzmann distribution.

These approaches can only be applied within the limit defined by the T/J_2 and J_1/J_2 ratios, for $|J_2| > |J_1|$. We have evaluated this limit in a small system whose exact magnetic behavior is known. The system that has been chosen for this purpose consists of the quantum Rad$-$Mn$^{II}-$Rad unit coupled with the only manganese(II) ion (J_1) through one radical center. In the last step, we can consider either quantum spin moments or a classical spin approach. For this model, we have obtained a J_1 value that allows us to reproduce the theoretical behavior in the $|T/J_2| > 0.01$ range (J_2 (K)). The deviation (<2%) from the theoretical J_1 value has been used to determine the J_1/J_2 limit. The limits for approaches 1$-$3 are 0.02, 0.05, and 0.02, respectively, when we use a classical spin approach. However, when J_1 is introduced in the framework of a quantum spin system, the J_1/J_2 limit takes larger values (0.25 for approach 1 and 0.45 for approach 2). These results show that the 3/2 spin moment is not long enough to be considered as a classical spin.

In the present work, we have used the simplest approaches (1 and 3), and similar results have been found. The effective spin of the Rad$-$Mn$^{II}-$Rad unit and the spin moment of the manganese(II) ion have been considered as classical spins. So, following Fisher's work, we have deduced a classical spin S_a-S_b regular chain law.[34] To check this law, a classical Monte Carlo simulation has been carried out.[35] Using $H = -JS_iS_j$ as the isotropic exchange coupling Hamiltonian, the least-squares analysis (300$-$8 K) of the $\chi_M T$ data for the compound using this approach leads to g(Rad) = 2.0017 ± 0.0015, g(Mn) = 2.0017 ± 0.0015, $J_1 = -0.622 \pm 0.022$ cm^{-1}, $J_2 = -203 \pm 3$ cm^{-1}, and an agreement factor $R = \sum(\chi_{M,\text{exptl}}(i) - \chi_{M,\text{calcd}}(i))^2/\sum(\chi_{M,\text{calcd}}(i))^2$, equal to 2.9×10^{-5}. We note that the values obtained for the J_1 and J_2 constants are coherent with the T/J_2 and J_1/J_2 limits of the considered approaches. The J_1 antiferromagnetic interaction is weaker than that reported in the literature.[33] This is probably due to (i) the fact that the interaction between the radicals through the manganese(II) ion has been neglected or/and (ii) possible structural differences with the previous complexes.

To check the approaches used in the fit procedure, we have simulated the magnetic curves for $J_1 = -0.622 \pm 0.022$ cm^{-1} and $J_2 = -203 \pm 3$ cm^{-1} by exact diagonalization and by quantum Monte Carlo (QMC) simulation of a ring within 8 and 100 paramagnetic sites, respectively. The QMC simulation has been carried out using the modified decoupled cell proposed by Miyazawa et al.[36] In this case the one-dimensional system has been decomposed in cells containing seven neighboring sites. The agreement among these two simulations, the fitted curve, and the experimental data is very good. So we can conclude that our results are correct and approaches 1$-$3 are useful to analyze the magnetic properties of the complex system.

Concluding Remarks

Structural and magnetic properties have been described for a new complex engineered from a 2,2′-bipyridine ligand carrying two nitronyl nitroxide free radicals in the *meta* positions of the chelating core. The new compound is best described as a 1D chain in which the complexed biradical bridged two [Mn(hfac)$_2$] units connected to a neighboring biradical. The magnetic behavior of this complex is dominated by the strong antiferromagnetic interaction (J_2, J_3) due to the radical centers directly bound to the manganese(II) ions Mn2 and Mn3 ($J_2 = J_3 = -203 \pm 3$ cm^{-1}). A second significant and antiferromagnetic interaction (J_1) results from the coupling of the peripherical nitronyl nitroxide radicals with the central manganese(II) ions Mn1 coordinated to the bipyridine moiety ($J_1 = -0.622 \pm 0.022$ cm^{-1}). Qualitatively, the minimum found in the susceptibility measurements closely matches the value expected for a ground spin state $S = 3/2$ added to a spin $S = 5/2$ imported by the additional manganese center Mn1. The susceptibility increase found at cryogenic temperature may be viewed then as the result of a fictive ferromagnetic coupling related to the true antiferromagnetic coupling J_1 between the pseudospin $S = 3/2$ and spin $S = 5/2$ of Mn1.

This novel chain complex documents the intimate relationship between magnetic properties and structural features and is a typical example of direct exchange. We are now engaged in a program where we expect to block the bipyridine center by a nonmagnetic group to generate the magnetic chain. Deprotection of the central bipyridine fragment would provide the opportunity to chelate a different magnetogen transition metal with a known octahedral, square planar, or tetrahedral geometry.

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

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