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# Synthesis, Structure and Magnetic Properties of a Chiral One-Dimensional Molecular-Based Magnet

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A novel chiral organic radical 2-{4'-((S)-2''-methylbutoxy)phenyl}-4,4,5,5-tetramethylimidazole-1-oxyl-3-oxide (**1**) and its metal complex,  $[\mathbf{1} \cdot \text{Mn(II)(hfac)}_2]_n$  were synthesized and characterized. The radical **1** crystallizes in the orthorhombic space group  $P2_12_12_1$  (No. 19) with  $a = 11.494(3)$  Å,  $b = 25.328(3)$  Å,  $c = 6.1281(5)$  Å,  $V = 1748.0(4)$  Å<sup>3</sup>. The complex  $[\mathbf{1} \cdot \text{Mn(II)(hfac)}_2]_n$  crystallizes in the same space group with  $a = 14.081(1)$  Å,  $b = 15.940(1)$  Å,  $c = 16.075(1)$  Å,  $V = 3608.1(4)$  Å<sup>3</sup>. X-ray crystal structure analysis of the complex revealed the formation of a helical-chain structure. The oxygen atoms of the radical **1** are ligated to two different manganese ions in *cis* position and exhibit the  $\Delta$  configuration in  $[\mathbf{1} \cdot \text{Mn(II)(hfac)}_2]_n$ . The magnetic measurements revealed that this chiral complex behaves as a ferrimagnet below  $T_C = 4.5$  K. It is characterized by a strong intrachain exchange correlation, the ratio between the intrachain and interchain exchange interactions being about  $10^{-5}$ .

**Keywords:** chiral magnet; triplet chiral organic radical; molecule-based magnet; high spin molecule

## Introduction

The design of assembled metal complexes with interesting magnetic, optical or electrical properties is one of the major challenges in molecular magnetism.[1] We have developed a strategy of using  $\pi$ -conjugated high-spin

oligonitroxide radicals which can be used as bridging ligands for paramagnetic transition metal complexes in order to assemble and align the electron spins on a macroscopic scale.[2-7] This strategy can successfully be employed for synthesis of new chiral molecular-based magnetic materials when one or both of the building blocks are chiral.

Novel magneto-optical phenomena have been theoretically predicted[8,9] and observed in chiral paramagnetic materials which are transparent for light.[10] However few examples of chiral molecule-based magnetic materials are known by far.[1,6,11-14] To get more insight in their properties it is therefore important to construct and study such materials. This manuscript concerns with synthesis, X-ray crystallographic structure analysis and magnetic properties of a novel chiral one-dimensional manganese(II) complex prepared from a chiral organic radical.

### **Synthesis**

#### **2-{4'-((S)-2''-methylbutoxy)phenyl}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide chiral monoradical**

The chiral radical **1** was synthesized according to the reported procedure.[15] m.p. 84.2 °C, MS ( $m/z$  = 319), HRMS  $m/z$  found 319.2006 calcd for  $C_{18}H_{27}O_3N_2$  319.2022, EPR (9.4522 GHz, hexane)  $g$  = 2.0058,  $a_N$  = 7.63 G, UV-Vis (hexane)  $\lambda_{max}(\epsilon)$  = 283 (19200) nm, 366 (11700) nm,  $[\alpha]_{405}^{25}$  = 202.89° ( $c$  = 0.0138,  $CH_2Cl_2$ ).

#### **[1•Mn(II)(hfac)<sub>2</sub>]<sub>n</sub> complex**

A *n*-heptane solution of 0.3 g of  $Mn(hfac)_2 \cdot 2H_2O$  was refluxed to be dehydrated and mixed with 0.2 g of the radical **1** in dichloromethane. The solution was evaporated and stored at -30 °C. Deep brown block crystals were obtained. Anal. Calcd for  $MnC_{28}H_{29}O_7F_{12}N_2$ : C, 42.65; H, 3.71; N, 3.55. Found: C, 42.19; H, 3.37; N, 3.47.

### **X-ray crystal structure analysis**

X-ray structure analysis for **1**; Reflection intensities were measured at -100 °C on a Rigaku RAXIS-IV imaging plate area detector; a Lorentz polarization correction was applied. Crystal data for **1**;  $C_{18}H_{27}O_3N_2$ ,  $M_w$  = 319.43, crystal size, 0.20 0.10 0.05 mm<sup>3</sup>; Orthorhombic,  $a$  = 11.494(3) Å,  $b$  = 25.328(3) Å,  $c$  = 6.1281(5) Å,  $V$  = 1748.0(4) Å<sup>3</sup>, Space Group  $P2_12_12_1$

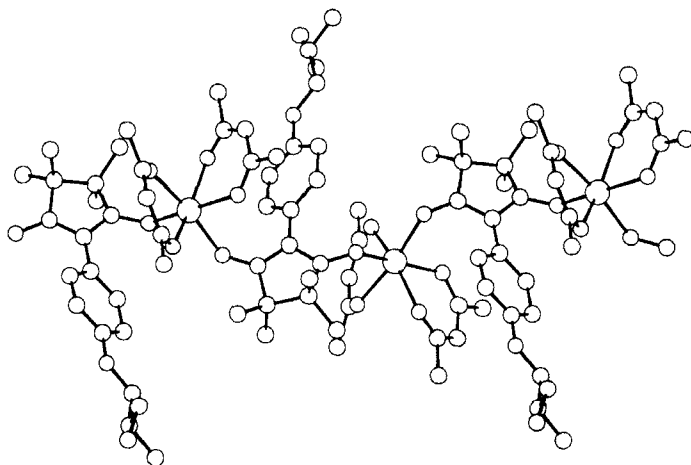
(No. 19),  $Z = 4$ ,  $D_c = 1.189 \text{ g cm}^{-3}$ , absorption coefficient =  $0.81 \text{ cm}^{-1}$ , Reflections = 1389, ( $I > 2.00\sigma(I)$ ),  $R$  ( $R_w$ ) = 0.067 (0.083), parameters = 208, Maximum and minimum residual electron densities  $0.30 \text{ e}^{-}/\text{\AA}^3$  and  $-0.41 \text{ e}^{-}/\text{\AA}^3$

X-ray structure analysis for  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$ ; Reflection intensities were measured at  $25^\circ\text{C}$  with  $\omega$  scan mode on a Bruker SMART CCD diffractometer; an empirical absorption correction were applied. Crystal data for complex  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$ ;  $\text{MnO}_7\text{C}_{28}\text{N}_2\text{F}_{12}\text{H}_{29}$ ,  $M_w = 788.47$ , crystal size,  $0.46 \times 0.23 \times 0.22 \text{ mm}^3$ ; Orthorhombic,  $a = 14.081(1) \text{ \AA}$ ,  $b = 15.940(1) \text{ \AA}$ ,  $c = 16.075(1) \text{ \AA}$ ,  $V = 3608.1(4) \text{ \AA}^3$ , Space Group  $P2_12_12_1$  (No. 19),  $Z = 4$ ,  $D_c = 1.452 \text{ g cm}^{-3}$ , absorption coefficient =  $0.471 \text{ mm}^{-1}$ , Reflections = 8695, ( $I > 2.00\sigma(I)$ ),  $R$  ( $R_w$ ) = 0.0690 (0.1692). Absolute structure parameter =  $-0.03(3)$ , parameters = 451, Maximum and minimum residual electron densities  $0.477 \text{ e}^{-}/\text{\AA}^3$  and  $-0.393 \text{ e}^{-}/\text{\AA}^3$

### Results and discussion

The molecular structure of  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$  is depicted in FIGURE 1. The asymmetric unit of  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$  consists of one Mn(II) ion, two (hfac) anions and one chiral radical **1**. The manganese(II) ion has an octahedral coordination environment with four oxygen atoms of the two (hfac) anions and two oxygen atoms of two different nitronyl nitroxide molecules. As a result, the Mn(II) ions and the chiral radicals form a one-dimensional structure along the crystal  $a$ -axis. The oxygen atoms of the radical are bound to the Mn(II) ion in *cis*-coordination to each other. A detailed description of the coordination sphere of the Mn(II) ion must take into account the possible configurations resulting from the *cis*-coordination arrangement, which can lead to  $\Delta$  or  $\Lambda$  configurations. Because of the use of a chiral ligand, the complex  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$  crystallizes in a chiral space group and no  $\Lambda$  chirality of the Mn(II) exists in this crystal: the metal centers exhibit  $\Delta$  configuration only. Since no inversion centers are present in this space group, the chains have a helical structure and are isotactic as all the units. The crystal lattice of  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$  as a whole is chiral.

The circular dichroism spectra of  $[\mathbf{1}\cdot\text{Mn(II)(hfac)}_2]_n$  confirmed the chiral structure of this complex in the crystalline state.[15] The measurements of the



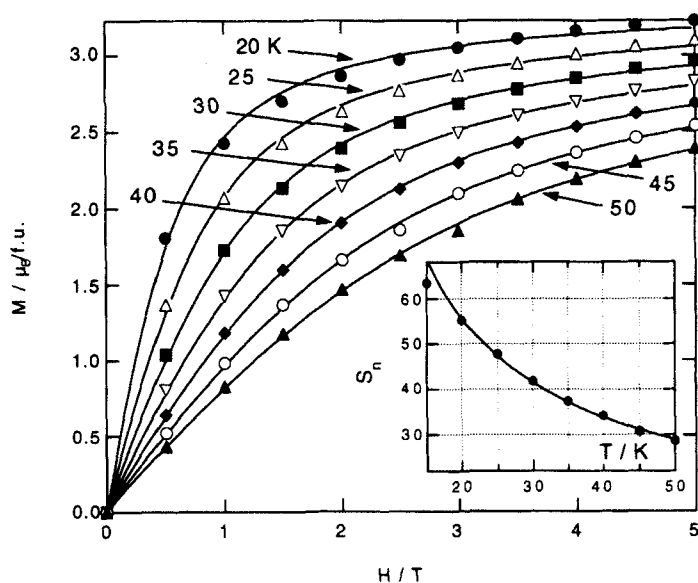
**FIGURE 1** The X-ray crystal structure of the complex of  $[1\bullet\text{Mn(II)(hfac)}_2]_n$ . Hydrogen atoms and fluorine atoms are omitted for clarity.

paramagnetic susceptibility have shown that this complex is characterized by a very strong intrachain exchange interaction between the spins of Mn(II) and the monoradical **1**,  $J/k = -435$  K, while the interchain interaction is very low  $J'/k \sim 10^{-3}$ . The ordering temperature was determined to be about 4.5 K. As can be seen from FIGURE 2, the magnetization curves of  $[1\bullet\text{Mn(II)(hfac)}_2]_n$  remain substantially nonlinear far above the Curie point (4.5 K).

In FIGURE 2 the solid lines are theoretical fits to the experimental data by the Brillouin function  $g\mu_B S_n B_s(g\mu_B H / kT)$ , where  $H$  is the external field. In the fits  $S_n$ , the value of the spin per f.u., was taken 2 B. Hence  $S_n = nSu$  can characterize the average length the correlated spins make up at the given temperature. The inset in FIGURE 2 shows the temperature variation of this quantity correlate. Down to 15 K it can be well approximated as  $S_n = 2 + 500T^{-4/3}$ .

In summary, a novel chiral organic radical and its Mn(II) complex were prepared and a chiral one-dimensional hybrid (heterospin) chain was realized. This complex has a helical-chain structure and is characterized by chiral ( $S$ )

carbon centers. The magnetic measurements have revealed that this complex shows a strong intrachain exchange correlation.



**FIGURE 2.** The magnetization curves of the chiral complex  $[1\cdot\text{Mn(II)}(\text{hfac})_2]_n$  measured at different temperatures in the paramagnetic range. The inset shows the temperature variation of the correlation length  $S_n$  (see text).

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