One-Dimensional Ferrimagnetic Chains with Weak Ferromagnetic Interchain Interaction in a 1 : 1 Manganese(II) Bis(hexafluoroacetylacetonate) Complex with Bis[3-*tert*-butyl-5-(*N*-oxy-*tert*-butylamino)phenyl] Nitroxide

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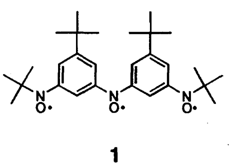
Black block crystals of $[Mn(hfac)_2 \cdot \mathbf{1}]_n$ obtained from a solution of anhydrous manganese(II) bis(hexafluoroacetylacetonate) $\{Mn(hfac)_2\}$ and bis[3-*tert*-butyl-5-(*N*-oxy-*tert*-butylamino)-phenyl] nitroxide (**1**) in *n*-hexane/ether were found to have a one-dimensional chain structure by the coordination of the terminal nitroxide groups of **1** with two different Mn ions and undergo a transition into a spin-ordered state at 11 K.

Recently, we introduced a strategy of using π-conjugated polynitroxide radicals with high-spin ground states as bridging ligands for magnetic metal ions in order to assemble and align the electron spins on a macroscopic scale.[1,2] *m*-Phenylenebis(*N*-*tert*-butylnitroxide) **2** with a triplet ground state formed with bis(hexafluoroacetylacetonato)manganese(II) $Mn(hfac)_2$ a polymeric one-dimensional chain.[3] An assembly of these chains became a metamagnet below 5.5 K by virtue of a weak interchain interaction. 1,3,5-Tris{*p*-(*N*-oxy-*tert*-butylamino)-phenyl}benzene **3** formed with $Mn(hfac)_2$ a polymeric complex $[\{Mn(hfac)_2\}_3 \cdot \mathbf{3}_2]_n$ with a stacked two-dimensional network sheet structure.[4] The metal complex did undergo transition to a spin-ordered phase at 3.4 K. While the short-range antiferromagnetic coupling between the d^5 manganese ion and the attached nitroxide radical center was strong, the weak intramolecular ferromagnetic coupling of $J/k_B = 6.8$ K within the molecule of **3** was considered to be responsible for the observed low transition temperature. We therefore employed in this study bis{3-*tert*-butyl-5-(*N*-oxy-*tert*-butylamino)phenyl} nitroxide **1** that has a stronger J/k_B value of 240 K.[5] Furthermore, the two terminal nitroxide radicals are expected to ligate to two different manganese ions to form a one-dimensional chain with the alternating triradicals and Mn ions as in **2**. The slightly hindered middle nitroxide radical center would then serve as a bridging ligand between the neighboring chains.



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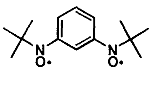

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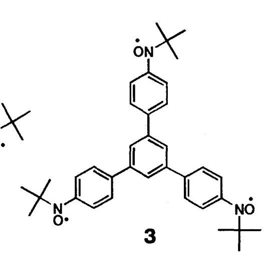

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A *n*-heptane solution of 7.5 mg of $Mn(hfac)_2 \cdot 2H_2O$ was refluxed to be dehydrated and mixed with 10 mg of triradical **1** in diethyl ether. The solution was evaporated completely and the residue was dissolved in 0.1 ml of diethyl ether and 0.4 ml of *n*-hexane. Black block crystals were obtained at -10°C in 2 days. A black block single crystal of $[Mn(II)(hfac)_2 \cdot \mathbf{1} \cdot n\text{-}C_6H_{14}]_n$ in approximate dimensions 0.30 × 0.40 × 0.20 mm was mounted on a glass fiber. Diffraction data were obtained with 2θ (max.) = 55.1° at 22 °C. The structure was solved in $P2_1/c$ to give crystal data: $C_{38}H_{44}N_3O_7F_{12}Mn \cdot C_6H_{14}$, MW = 1023.88, monoclinic, space group $P2_1/c$ (No. 14), a = 10.137(3) Å, b = 19.426(5) Å, c = 27.187(7) Å, β = 95.21(2)°, V = 5331(2) Å^3, and D_X = 1.275 g/cm^3 for Z = 4. Non-hydrogen atoms were refined anisotropically. Refinement converged at R = 0.098 and RW = 0.096 for 2764 unique reflections, with $I > 3\sigma(I)$ and 604 variables. Since the anisotropic refinement of the carbon atoms of the disordered *n*-hexane molecules was difficult, it was not possible to improve the R values. Crystals of other compositions and morphologies were obtained from *n*-heptane/chloroform.[7]

The crystal structure of the complex thus obtained revealed that the Mn(II) ion has an octahedral coordination with the four oxygen atoms of two hfac anions and the two oxygen atoms of the terminal nitroxide groups of two different molecules of **1**. A one-dimensional zig-zag chain is formed by alternation of the Mn ion and triradical **1** (Figure 1). Contrary to our expectation, the middle nitroxide radical of **1** did not take part in the coordination with any Mn ion. A disordered hexane molecule is contained in each unit cell. On the basis of the spin density known to be rather localized on the N-O moieties[4] and the observed intermolecular distances between them, the strongest interchain interaction is judged to arise from the N(*tert*-Bu)O• --- N(*tert*-Bu)O• interaction with the distances of 4.86 Å between he neighboring chains. This type of interaction is suggested to be antiferromagnetic as dictated by the McConnell theory.[8]

The magnetic susceptibility of unoriented microcrystalline samples of $[Mn(II)(hfac)_2 \cdot \mathbf{1} \cdot n\text{-}C_6H_{14}]$ was measured on a Quantum Design MPMS2 SQUID susceptometer/magnetometer. The temperature dependence of the $\chi_{mol}T$ obtained at a field of 5000 Oe is given in Figure 2.[9] The $\chi_{mol}T$ value of 2.42 at 300 K is slightly larger than a theoretical value of 2.25 for antiparallel spins of two 1/2 spins of organic radicals and one 5/2 spins of d^5 Mn(II) and non-interacted one 1/2 spins of middle nitroxide. The $\chi_{mol}T$ value decreased with decreasing temperature and started to increase after reaching a minimum at 114 K (Figure 2 (Inset)). When the measurement was carried out in a much lower field, the magnetic susceptibility value showed a sharp rise at 11

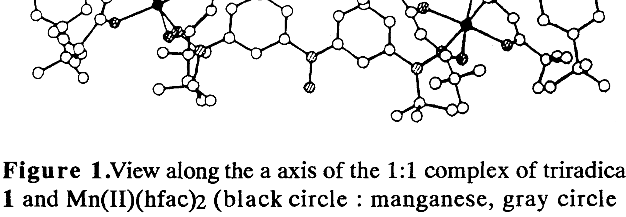

Figure 1. View along the a axis of the 1:1 complex of triradical **1** and $Mn(II)(hfac)_2$ (black circle : manganese, gray circle : oxygen and nitrogen, and open circle : carbon and fluorine).

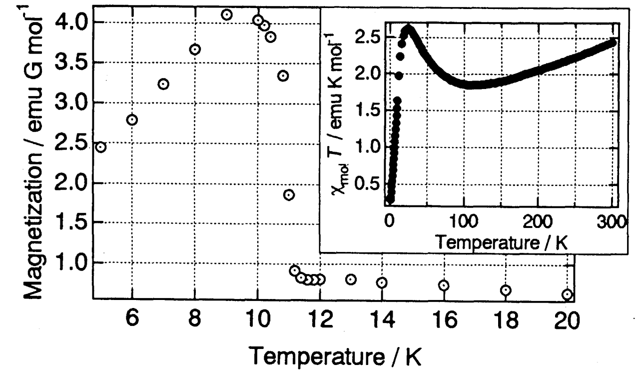

Figure 2. The observed magnetization versus T plots for the complex Mn(II)(hfac)$_2$•**1**•n-C$_6$H$_{14}$ measured at a magnetic field of 5 Oe (○). The inset shows the $\chi_{mol}T$ versus T plots for the complex measured at 5000 Oe.

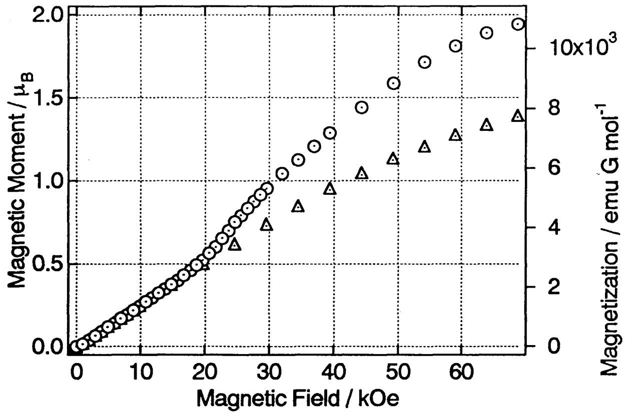

Figure 3. The observed magnetization curve for the complex Mn(II)(hfac)$_2$•**1**•n-C$_6$H$_{14}$ measured at 1.8 K (○) and 15.0 K (△).

K and then decreased with decreasing temperature (Figure 2). The ZFC magnetization showed also a sharp cusp at ca. 11 K. The magnetization at 1.8 K revealed metamagnetic behavior (Figure 3). Namely, while the response of the magnetization was not sensitive to the weak applied magnetic field below ca. 20 000 Oe, a behavior characteristic of an antiferromagnet, a sharp rise and approach to saturation of magnetization characteristic of a ferromagnet was observed at higher applied magnetic field (Figure 3). The magnetization at 1.8 K under 70 000 Oe reached a value of ca. 2 μ_B which is not in conflict with a theoretical saturation value of 2 μ_B (5/2 - 3/2 = 2/2) for the antiferromagnetic interaction between the manganese(II) ion and **1** in [Mn(II)(hfac)$_2$•**1**•n-C$_6$H$_{14}$].

It is concluded that 1-D hybrid-chain consisting of ferro- and antiferromagnetic couplings within the triradical and between the 2p and 3d spins, respectively, has been realized. The interaction between the 1-D chains appears to be weakly antiferromagnetic, making the complex, an assembly of the 1-D chains, a molecule-based metamagnet (Figure 4).[8] Thus, while the middle nitroxide group of triradical **1** was less reactive as a ligand to Mn(II) ion than the two terminal ones and the expected bridging of the 1-D chains was not attained, π-conjugated polynitroxide radicals with high-spin ground states appear promising as bridging ligands for magnetic metal ions in constructing ordered spins and relevant magnetic properties.

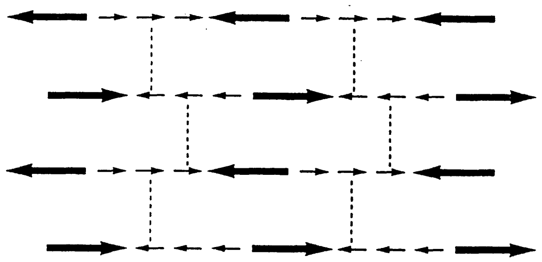

Figure 4. Schematic drawing of the magnetic structure of **1**•Mn(II)(hfac)$_2$. Broken lines show the N($tert$-Bu)O• - N($tert$-Bu)O• antiferromagnetic interaction between the ferro/ferrimagnetic 1-D chains.

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6 The preparation of **1** was improved by using n-butyllithium in place of $tert$-butyllithium for monolithiation of 1,3-dibromo-5-$tert$-butylbenzene. Six equivalents of tetrabutylammonium fluoride trihydrate were used to deprotect the disilylated dihydroxylamines.

7 To be published elsewhere.

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9 Application of Curie-Weiss law to the temperature dependence of χ_{mol} gave C = 7.16 emu K mol^{-1} and θ = -44.2 K in the range 180-300 K and C = 5.60 emu K mol^{-1} and θ = +1.8 K in the range 30-100 K.