

One-dimensional Ferro- and Ferri-magnetic Chains made of an Alternating Array of 1,3-Bis(*N*-*tert*-butyl-*N*-oxyamino)benzene and Mn^{II}(hfac)₂ (Hhfac = Hexafluoroacetylacetonate)

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A black monoclinic crystal of 1,3-[Bu^tN(O·)]₂C₆H₄·Mn^{II}(hfac)₂, for which the formation of one-dimensional chains by ligation of the bisnitroxide radical serving as a bidentate ligand to Mn^{II}(hfac)₂ has been disclosed by an X-ray crystal structure analysis, undergoes transition to a metamagnet at 5.5 K.

Construction of molecular based magnetic materials which have a well-defined one- or two-dimensional structure is a scientific subject of increasing interest.¹ Heterospin systems consisting of transition metal ions and organic free radicals as ligands constitute one of the mainstreams of such studies. Several of these materials have been established to have finite critical temperatures for undergoing transition to ferro- and/or ferri-magnets.² The ligands employed are often organic monoradicals that have two ligating sites, e.g. semiquinones³ and nitronylnitroxides.²

We have introduced a new strategy of employing π -conjugated polynitroxides as ligands in which the spins interact ferromagnetically ($J_1 > 0$) (Fig. 1).⁴ The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighbouring spins may be readily tuned by this strategy. We report here a thus fabricated one-dimensional metamagnet composed of bisnitroxide radical **1** and manganese(II) hexafluoroacetylacetonate, Mn^{II}(hfac)₂. The diradical **1** has been established to have a triplet ground state with a large intramolecular ferromagnetic coupling of $J_1/k_B > 300$ K,⁵ where J_1 is defined as an intramolecular exchange parameter in the Heisenberg Hamiltonian $H = -2J_1 S_a \cdot S_b$ for the spins S_a and S_b in the same molecule of diradical **1**.

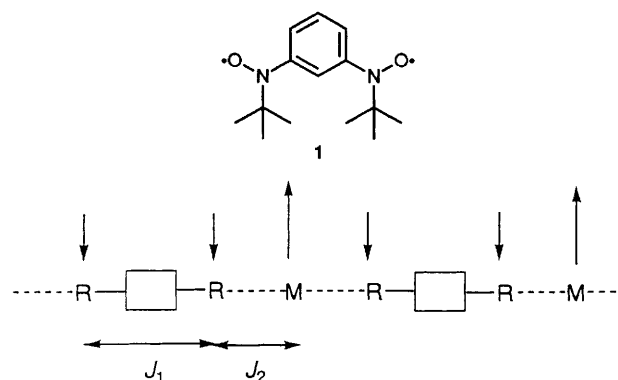


Fig. 1 Schematic drawing of a one-dimensional chain formed by transition metal M to which ferromagnetically coupled ($J_1 > 0$) diradicals are ligated in an antiferromagnetic fashion

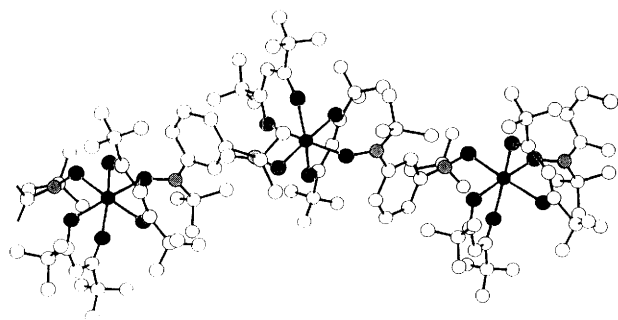


Fig. 2 View of a one-dimensional chain formed by bisnitroxide **1** and Mn^{II}(hfac)₂

The complex **1**·Mn^{II}(hfac)₂ was obtained by dissolving 12 mmol of Mn(hfac)₂·H₂O in a mixture of 1 ml of acetone and 10 ml *n*-heptane to which were added 12 mmol of **1** in 10 ml of *n*-heptane. The solution was concentrated under reduced pressure to ca. 5 ml to give black needles from a deep brown solution.

A black needle single crystal of **1**·Mn^{II}(hfac)₂ was used to determine the X-ray crystal structure† of the complex, which revealed that the manganese(II) ion has an octahedral coordination with four oxygen atoms of two hfac anions and the two oxygen atoms of the two nitroxide groups. The latter are bound to the Mn^{II} ion in *cis*-configuration. As a result, the Mn^{II} ion and the diradical molecules form a zigzag one-dimensional polymeric chain structure (Fig. 2). On the basis of the spin density known to be rather localized on the N–O moieties^{5c,6} and the observed intermolecular distance between them, the strongest interchain interaction is judged to arise from the NBu^tO· ... F ... NBu^tO· interaction with distances of 4.95 and 4.97 Å. This type of interaction is suggested to be antiferromagnetic as dictated by McConnell's theory⁷ and the superexchange mechanism through the fluorine atom.

The temperature dependence of the molar magnetic susceptibility χ for a microcrystalline sample of **1**·Mn^{II}(hfac)₂ was investigated at several magnetic field strengths on a SQUID susceptometer. In the magnetic field of 5000 Oe, the product χT of the molar susceptibility and temperature increased steadily with decreasing temperature, reached a maximum at 8.5 K, and then decreased [Fig. 3 (inset)]. The observed χT value of 2.11 emu K mol⁻¹ at 300 K is slightly (but not much) larger than the theoretical value of 1.88 emu K mol⁻¹ for a model in which the interaction between the Mn^{II} and the directly attached nitroxide group is antiferromagnetic and the two spins within the molecule of **1** are not yet ordered. Application of Curie–Weiss law to the temperature dependence of χ gave a Curie constant C of 1.9 emu K mol⁻¹ and a Weiss constant θ of 40 K in the range 50–350 K. When the measurement was carried out in the much lower field of 1 Oe, the magnetic susceptibility value showed a sharp rise at 5.5 K

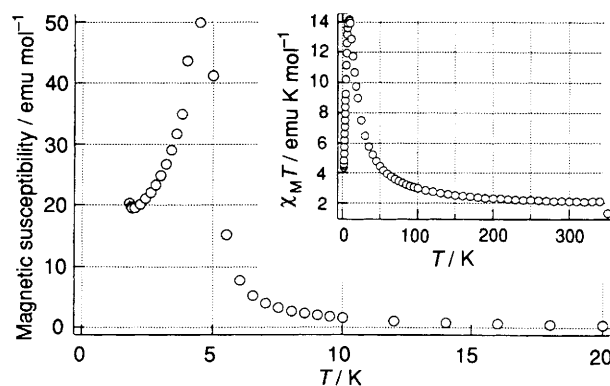


Fig. 3 Molar magnetic susceptibility χ_M vs. T plots for the complex **1**·Mn^{II}(hfac)₂ measured at 1 Oe. χT vs. T plots for the complex measured at 5000 Oe are given in the inset.

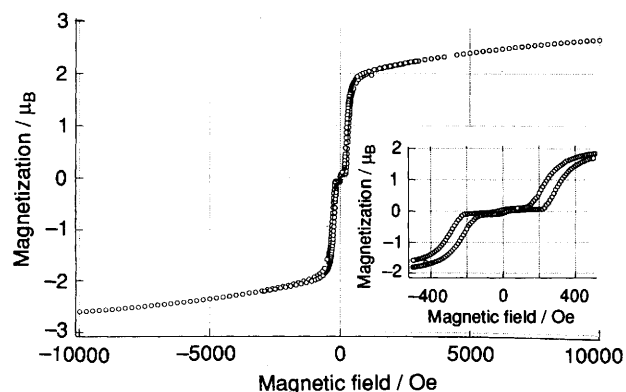


Fig. 4 Field dependence of the magnetization of $1\text{-Mn}^{\text{II}}(\text{hfac})_2$ measured at 1.8 K

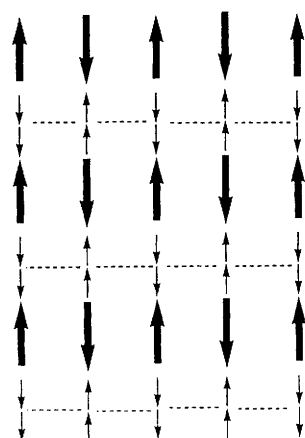


Fig. 5 Schematic drawing of the magnetic structure of $1\text{-Mn}^{\text{II}}(\text{hfac})_2$. Broken lines show the $\text{NBu}^{\text{O}} \cdots \text{F} \cdots \text{NBu}^{\text{O}}$ antiferromagnetic interaction between the ferro/ferrimagnetic one-dimensional chains.

and then decreased with decreasing temperature (Fig. 3). The ZFC magnetization shows also a sharp cusp at ca. 5 K. Magnetization at 1.8 K revealed metamagnetic behaviour (Fig. 4). Namely, while the response of the magnetization was not sensitive to the weak applied magnetic field below ca. 200 Oe, behaviour characteristic of an antiferromagnet, a sharp rise and approach to saturation of magnetization characteristic of a ferromagnet was observed at higher applied magnetic field with measurement on a Faraday balance [Fig. 4 (inset)]. A saturation magnetization value of ca. $3 \mu_{\text{B}}$ was reached at 1.8 K at 30000 Oe. When the interaction between the manganese(II) ion and **1** is antiferromagnetic ($J_2 < 0$ in Fig. 1), the value of $1\text{-Mn}^{\text{II}}(\text{hfac})_2$ is expected to be $3 \mu_{\text{B}}$ ($5/2 - 2/2 = 3/2$), in good agreement with the observed value.

It is concluded that a one-dimensional hybrid chain consisting of ferromagnetic ($J_1 > 0$) and antiferromagnetic ($J_2 < 0$ in Fig. 1) couplings has been realized. The interaction between the one-dimensional chains is expected to be weakly antiferromagnetic, making the $1\text{-Mn}^{\text{II}}(\text{hfac})_2$ complex, an assembly of the one-dimensional chains, a molecular-based metamagnet (Fig. 5).⁸

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Footnote

† Crystal data for $1\text{-Mn}^{\text{II}}(\text{hfac})_2$: $\text{C}_{24}\text{H}_{24}\text{F}_{12}\text{MnN}_2\text{O}_6$, $M_{\text{w}} = 719.38$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.212(3)$, $b = 16.620(3)$, $c = 20.088(2)$ Å, $\beta = 98.46(1)^\circ$, $V = 3042(1)$ Å³, $D_{\text{c}} = 1.571$ g cm⁻³, $Z = 4$, crystal dimensions $0.30 \times 0.15 \times 0.95$ mm, $2\theta(\text{max}) = 55.1^\circ$ at 21 °C. All non-hydrogen atoms were refined anisotropically. Refinement converged at $R = 0.055$ and $R_{\text{w}} = 0.058$ for 3256 unique reflections, with $I > 3\sigma(I)$ and 434 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for authors, Issue No. 1.

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