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Magnetic Characterization of One-Dimensional Molecule-Based Metamagnet Made of $Mn(hfac)_2$ AND 1,3- BIS(N-OXY-tert-Butylamino)Benzene

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MAGNETIC CHARACTERIZATION OF ONE-DIMENSIONAL MOLECULE-BASED METAMAGNET MADE OF $Mn(hfac)_2$ AND 1,3-BIS(*N*-OXY-*tert*-BUTYLAMINO)BENZENE.

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Abstract Manganese bis(hexafluoroacetylacetonate), $Mn(hfac)_2$, reacts with 1,3-bis-(*N*-oxy-*tert*-butylamino)benzene, **1**, to give a 1:1 polymeric complex of formula $[Mn(hfac)_2 \bullet \mathbf{1}]_n$. An X-ray crystal structure analysis reveals that the manganese(II) ion and the molecule of **1** makes one-dimensional chains by ligation of the latter serving as a bis(monodentate) ligand to the former. A crystalline sample of the complex undergoes transition to a metamagnet at 5.5 K. In the ordered phase, it exhibits a large uniaxial magnetic anisotropy with the uniaxial anisotropy constant, K_{u1}, of 8.3×10^6 J m^{-3} by single crystal magnetic measurements.

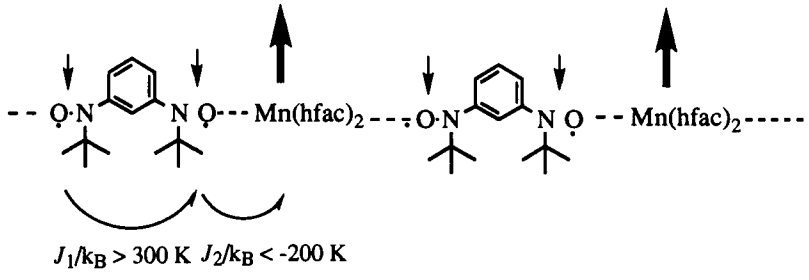
INTRODUCTION

Construction of molecule-based magnetic materials which have well-defined one-, two- or three-dimensional magnetic structure is a scientific subject of increasing interest [1]. Some nitroxide radicals have Lewis basicity and serve as ligands to magnetic metal ions such as copper(II) through the oxygen atoms [2]. If an organic free radical carries two ligating sites as in semiquinones and Ullman's nitronyl nitroxides, a one-dimensional chain polymer or a macrocycle is formed with coordinatively doubly unsaturated metal ions [3]. We have introduced a new strategy of employing π-conjugated polynitroxides as bridging ligands in which the spins interact ferromagnetically [4]. The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighboring spins may be readily tailored by this strategy. In this paper we concentrate on a one-dimensional (1-D) chain made of manganese(II) bis(hexafluoroacetylacetonate), Mn(II)$(hfac)_2$, and 1,3-phenylenebis(nitroxides) **1** (see Chart I). Depending on the nature of the additional interchain interactions, the chain polymers are expected to become an antiferromagnet, metamagnet, or ferri/ferromagnet. The results obtained hereby will be of use in establishing

a design strategy for tailored 3-D magnetic structures with high transition temperature on the basis of magnetic metal ions and high-spin organic polyradicals.

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 coupling parameter in the Heisenberg Hamiltonian: $H = -2J_1S_a \cdot S_b$, for the spins S_a and S_b in the same molecule of diradical **1**. The exchange coupling between the Mn(II) ion and the nitroxide radical is usually antiferromagnetic ($J_2 < 0$), because the 3d orbital of d^5 Mn(II) and 2p orbital of the nitroxide have a considerable overlap in the coordination bond .

Chart I



EXPERIMENTAL

Synthesis of the Complex

It was carried out as reported previously [4b].

X-ray Crystal Structure Analysis

A black needle single crystal of [Mn(II)(hfac)$_2$•**1**] in approximate dimensions 0.30 mm × 0.15 mm × 0.95 mm was mounted on a glass fiber. Diffraction data were obtained with 2θ (max.) = 55.1 ° at 21 °C. The structure was solved in $P2_1/n$ to give the crystal data: $C_{24}H_{24}N_2O_6F_{12}Mn$, MW = 719.38, monoclinic, space group $P2_1/n$ (No. 14), a = 9.212(3) Å, b = 16.620(3) Å, c = 20.088(2) Å, β = 98.46(1) °, V = 3042(1) Å^3, and D_X = 1.571 g/cm^3 for Z = 4. All non-hydrogen atoms were refined anisotropically. Refinement converged at R = 0.055 and R_W = 0.058 for 3256 unique reflections, with $I > 3\sigma(I)$ and 434 variables.

Magnetic Susceptibility Measurements

Magnetic susceptibilities were measured between 1.8 to 350 K on a Quantum Design MPMS2 SQUID susceptometer in a field up to 1 T. An Oxford Instruments Faraday

magnetic balance system with a 7 T superconducting magnet was also used to obtain high-field data.

SQUID measurements of polycrystals. A crystalline sample (ca. 10 mg) of the complex was place in a Japanese pharmacopoeia #5 gel capsule . The background data of the cell were measured separately and subtracted from the sample-in-cell data.

Faraday balance measurements. A quartz sample cell was filled with a crystalline sample (ca. 10 mg) of the complex which was then glued with Nujol (ca. 20 mg). The background data for the cell and the same amount of Nujol were measured separately and subtracted from the sample-in-cell data.

SQUID measurements of single crystal. A single crystal of the complex in approximate dimensions 1 mm × 0.8 mm × 6 mm was mounted on a Quantum Design sample rotator M101B and C.

RESULTS AND DISCUSSION

Crystal Structure

The X-ray crystal structure of complex **1** revealed that the manganese(II) ion has an octahedral coordination with the four oxygen atoms of two hfac anions and the two oxygen atoms of the two nitroxide groups. The latters are bound to the Mn(II) ion in *cis*-configuration. As a result, the Mn ion and the diradical molecules formed a zigzag 1-D polymeric chain structure. Further inspection reveals that the *tert*-butylnitroxide groups are rotated out of the phenylene ring plane in a conrotatory manner and that each molecule of **1** in the crystal has C_2 symmetry. The 1-D polymeric chain is therefore isotactic as all molecules of the same chirality, i.e., R or S, reside in a given chain (FIGURE 1). The crystal lattice as a whole is achiral as an enantiomeric chain is present. The Mn(II) ions on the neighboring chains are separated at least by 9.2 Å. Since the spin density is localized on the N-O moieties [5c,6] and the observed

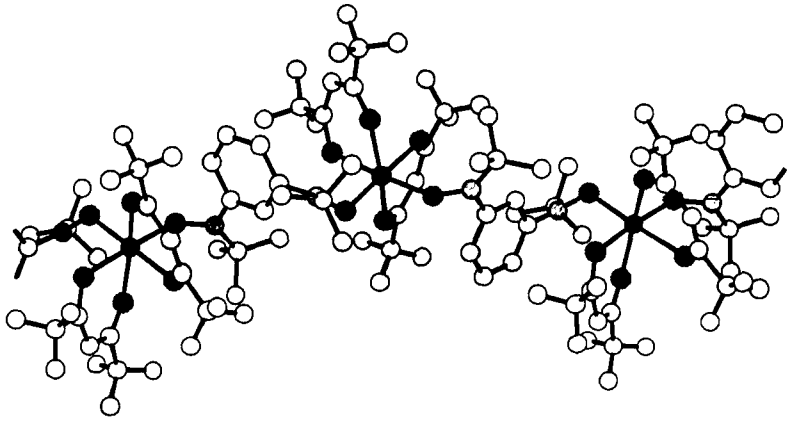


Figure 1. View of a 1-D chain formed by bisnitroxide **1** and Mn(II)(hfac)$_2$.

intermolecular distance is 4.96(1) Å, the strongest interchain interaction is judged to arise from the N(*tert*-Bu)O• --- F --- N(*tert*-Bu)O• interaction. This type of interaction is suggested to be antiferromagnetic as dictated by the McConnell's theory [7] and the superexchange mechanism through the fluorine atom.

Magnetic Properties

The temperature dependence of the molar magnetic susceptibility χ for the crystal of complex was investigated at several magnetic field strengths. The observed χT value of 2.11 emu K mol^{-1} for [Mn(II)(hfac)$_2$•**1**] at 300 K in the field of 5000 Oe 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 antiferromagnetically coupled and the ferromagnetic coupling between the two 2p spins within the ligand diradical molecules **1** is not strong enough to align them fully. In the magnetic field of 5000 Oe, the product χT of the molar susceptibility and temperature for **1** increased steadily, reached a maximum at 8.5 K, and then decreased with decreasing temperature (Figure 2). A minimum characteristic of a 1-D ferrimagnetic chain was assumed to be present at a temperature higher than 300 K. The ZFC magnetization at 0.5 Oe showed also a sharp cusp at ca. 5.5 K, suggesting the development of a higher order

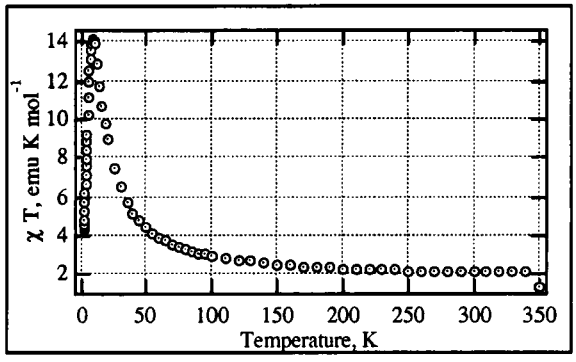


Figure 2. χT vs. T plots for the complex measured at 5000 Oe.

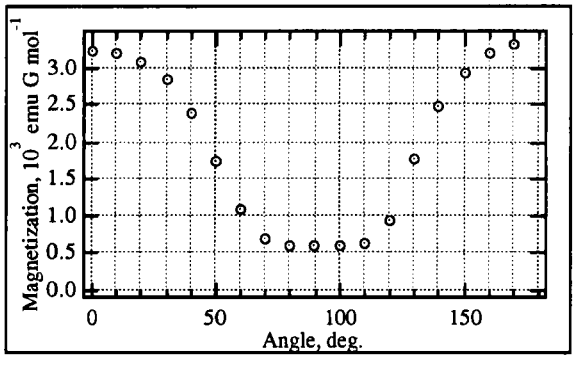


Figure 3. The angle dependence of the magnetization of a single crystal of this complex. Rotated along crystal *a* axis (O).

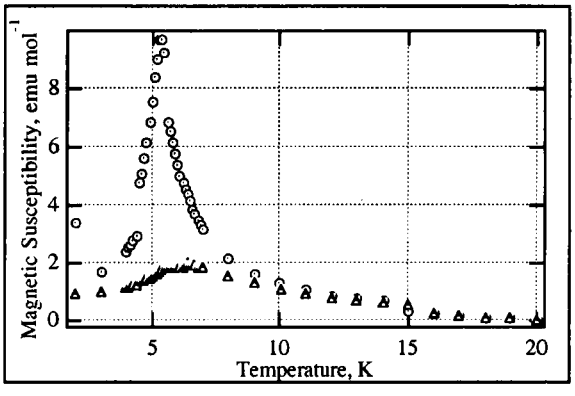


Figure 4. The temperature dependencies of the magnetic susceptibility of a single crystal of [Mn(II)(hfac)$_2$•**1**] along (O) and perpendicular to (Δ) the crystal *c* axis measured in 5 Oe.

antiferromagnetic interaction among the ferrimagnetic chains. The magnetization at 1.8 K revealed metamagnetic behavior. Namely, while the response of the magnetization was not sensitive to the weak applied magnetic field below ca. 200 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. Remnant magnetization was also detected.

A saturation magnetization value of ca. 3 μ_B was reached at 1.8 K at 30,000 Oe for the complex. When the interaction between the manganese(II) ion and ligand **1** is antiferromagnetic ($J_2 < 0$ in Chart I), the value of [Mn(II)(hfac)$_2$•**1**] is theoretically predicted to be 3 μ_B (5 / 2 - 2 / 2 = 3 / 2) which is in good agreement with the observed values.

The angular dependence of the magnetization of a single crystal of this complex was measured at a field of 1000 Oe and a temperature of 2.0 K, and revealed a conspicuous magnetic anisotropy (Figure 3). Temperature dependence of the magnetic susceptibility and a magnetization curve of a single crystal of the complex are shown in Figures 4 and 5, respectively. Thus the easy axis of magnetization is found to be along the *c* crystal axis; the dependence of magnetization on the strength of the external magnetic field applied perpendicular to the *c* axis is linear up to 8000 Oe. This results clearly indicates that the single crystal of this complex has a uniaxial magnetic anisotropy. Using a theory of angular dependence of magnetization for such systems (equation 1)[8], we obtained a uniaxial anisotropy constant of $K_{u1} = 8.3 \times 10^6$ J m^{-3}.

$$M = \frac{M_S^2}{2K_{u1}} H \qquad \text{(eq. 1)}$$

where, M is magnetization, H is applied magnetic field, and M_S is saturation magnetization and replaced with a theoretical value of 1.67×10^4 emu G mol^{-1}.

This result is in contrast with MnCu(pba) and MnCu(pbaOH) ferrimagnets in which the preferred spin orientation is not along the chain axis *b* but along the *c* axis [9]. The observed large anisotropic constant and the preference of the magnetization along the chain axis in [Mn(II)(hfac)$_2$•**1**] is considered to arise from stronger and weaker magnetic interactions within the chain and between the chains, respectively.

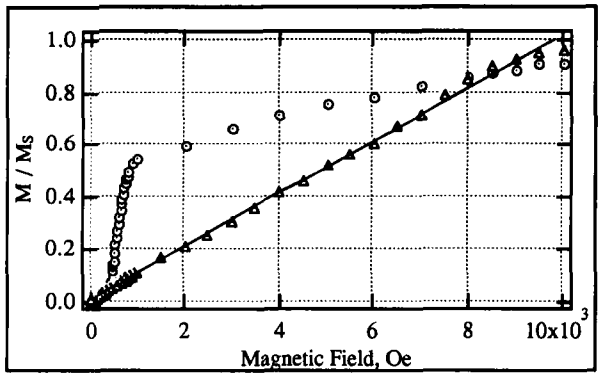


Figure 5. Field dependencies of the magnetization of a single crystal of [Mn(II)(hfac)$_2$•**1**] with the field applied along (O) and perpendicular to (Δ) the *c* axis at 1.8 K. Solid line is calculated by equation 1.

CONCLUSIONS

The 1-D hybrid-chains consisting of ferromagnetic ($J_1 > 0$) intra-ligand coupling and antiferromagnetic ($J_2 < 0$ in Chart I) coupling through the coordination bond have been realized. The interaction between the 1-D chains is weakly antiferromagnetic, making an assembly of the 1-D chains of [Mn(II)(hfac)$_2$•**1**] complex a molecule-based metamagnet (Figure 6)[10]. The single crystal of this complex has a large uniaxial magnetic anisotropy along *c* axis.

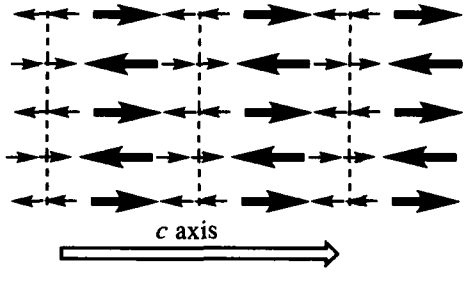


Figure 6. A schematic drawing of the magnetic structure of [Mn(II)(hfac)$_2$•**1**]. Broken lines show the N(*tert*-Bu)O• - F - N(*tert*-Bu)O• antiferromagnetic interaction between the ferrimagnetic 1-D chains. Solid lines show the ferromagnetic interchain interaction through the ligands.

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