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Synthesis and Characterization of a Chiral Molecule-Based Metamagnet Made by a Chiral Triplet Organic Radical and Transition Metal Ion

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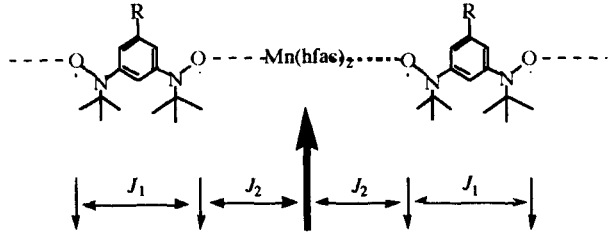
Crystals of $\{\mathbf{1}\bullet M(II)(hfac)_2\}_n$ (M = Mn, Cu) were obtained by mixing the 1,3-bis(*N-tert*-butylamino-*N*-oxyl)-5-{1-methyl-1-((*S*)-2-methylbutoxy)ethyl}benzene (**1**) and bis(hexafluoroacetylacetonato)M(II) $\{M(II)\bullet(hfac)_2\}$ in diethyl ether/*n*-heptane. A single crystal of $\{\mathbf{1}\bullet Mn(II)(hfac)_2\}n$ is triclinic, space group *P*1 (No. 1), with a = 11.0005(3) Å, b = 11.8183(4) Å. c = 17.7135(7) Å, α = 81.607(3)°, β = 84.801(3)°, γ = 63.516(2)°, V = 2038.3(1) Å^3, and D_X = 1.380 g/cm^3 for Z = 1. A single crystal of $\{\mathbf{1}\bullet Cu(II)(hfac)_2\}_n$ is triclinic, space group *P*1 (No. 1), with a = 11.2831(7) Å, b = 11.5615(7) Å, c = 18.0163(9) Å, α = 82.384(4)°, β = 74.242(4)°, γ = 61.826(5)°, V = 1993.9(2) Å^3, and D_X = 1.43 g/cm^3 for Z = 1. An X-ray crystal structure analysis revealed the formation of a helical one-dimensional polymeric structure. It not only contains a (*S*) chiral carbon center but also *(R) C2* chiral skeleton of the 1,3-bis(*N-tert*-butylamino-*N*-oxyl)benzene moiety. Each of the two aminoxyl radical centers are coupled ferromagnetically within the organic radical molecule and is coupled antiferromagnetically to the d^5 manganese(II) ions. The temperature dependence of the magnetization revealed that the heterospin system behaves as a metamagnet below 5.4 K.

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

INTRODUCTION

Construction of molecule-based magnetic materials which have well-defined structure such as dimensionality and/or chirality is scientific subject of increasing interest.[1,2] A strategy of using π-conjugated polyaminoxyl radicals with high-spin ground states as bridging ligands for magnetic metal ions has been studied. The dimensionality, and the structure of the complex and the sign and magnitude of the exchange coupling between the neighboring spins may be readily tuned by this strategy.[3-7] When we use a bidendate bisaminoxyl radicals as ligand and manganese(II) hexafluoroacetylacetonate, Mn(II)(hfac)$_2$, we can make one-dimensional complexes.[3,6] (Scheme I) The biradical **1H** (R = H) has been established to have a triplet ground state with large intramolecular ferromagnetic coupling of $J_1/k_B > 300$ K,[8] where



Scheme I

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 biradical **1H**. In this complex, two *tert*-butylaminoxyl groups are rotated out of the phenylene ring plane in a conrotatory manner; each **1H** molecule in the crystal has no symmetry element and therefore chiral, i.e., *R* or *S*. The 1-D polymeric chains are therefore isotactic as all units of the same chirality. The crystal lattice as a whole is achiral as an enantiomeric chain is present.[6] In this approach to molecular-based magnetic materials the versatility is given by the possibility to modify the R group of the radical.

In 1984 Barron and Vrbancich call "magneto-chiral dichroism" (MChD) for a link between natural and magnetic optical activity.[9] This penomena has been studied theoretically and experimentally.[8,9] Recent observation of the

MChD effect of tris(3-trifluoroacetyl-±-camphorato)europium (III) in the paramagnetic state stimulates us to synthesize molecule-based magnets having chiral carbon center.[10] There are few examples of molecule-based chiral magnet.[11] Here we report the construction of fully chiral molecule-based magnet which is made by π-conjugated chiral bisaminoxyl radical and transition metal ion.

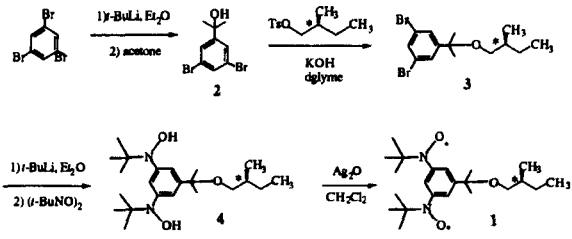
EXPERIMENTAL

Magnetic Susceptibility Measurement

Magnetic susceptibilities were measured between 1.8 to 300 K on a Quantum Design MPMS5S SQUID susceptometer. A crystalline sample of the complex was placed in a Japanese pharmacopoeia #5 gel capsule. The background data of the cell were measured separately and subtracted from the sample-in-cell data.

Synthesis

The synthetic route of the chiral diradical **1** illustrates in Scheme II.



Scheme II

A commercially available chiral starting material, (*S*)-2-methyl-1-butanol was used for synthesize of **1**. 1,3-dibromo-5-{1-methyl-1-((*S*)-2-methylbutoxy)ethylbenzene (**3**) was obtained by condensation of 2-(3,5-dibromophenyl)-2-propanol (**2**) and 1-(*S*)-2-methylbutyl toluenesulfonate. The precursor **4** was obtained as white powder. MS (*m/z* = 380), ^{1}H-NMR (270 MHz, $CDCl_3$) δ = 7.40 (bs, 2H), 7.05 (s, 1H), 6.88 (s, 2H), 2.8-3.0 (m,

2H), 1.5-1.7 (m, 1H), 1.4-1.5 (m, 2H),1.35 (s, 6H), 1.07 (s, 18H), 0.86 (s,3H), 0.83 (s,3H)

During the synthesis of **1**, CD spectra of compound **3** and **4** in dichloromethane were observed. These results are indicative of no racemization of the precursors during the reaction. Precursor **4** was oxidized by silver oxide in dichloromethane at 0 °C and purified by column chromatography on silica gel eluted with dichloromethane and ether. MS (*m/z* = 378), HRMS *m/z* found 378.2869 calcd for $C_{22}N_2O_3H_{38}$ 378.2882 EPR (9.4507 GHz, CH_2Cl_2) g = 2.0055, a_N = 13.1 G, UV-Vis (CH_2Cl_2) $\lambda_{max}(\varepsilon)$ 285 (20,200) nm

Synthesis of [1•Mn(II)(hfac)2]n

A *n* - heptane solution of 0.09 g of $Mn(hfac)_2{\bullet}2H_2O$ was refluxed to be dehydrated and mixed with 0.13 g of diradical **1** in dichloromethane. The solution was evaporated and stored at -30 °C. Deep brown block crystals were obtained.

Synthesis of [1•Cu(II)(hfac)2]n

Cu(II) complex was synthesized by similar procedure for Mn(II) complex using $Cu(hfac)_2{\bullet}2H_2O$.

X-ray crystal structure analysis

Crystal data for $[\mathbf{1}{\bullet}Mn(II)(hfac)_2]_n$: brown block; 0.10 × 0.15 × 0.05 mm^3; triclinic, space group $P\bar{1}$, a = 11.0005(3) Å, b = 11.8183(4) Å, c = 17.7135(7) Å, α = 81.607(3)°, β = 84.801(3)°, γ = 63.516(2)°, V = 2038.3(1) $Å^3$, Cu Kα radiation (λ = 1.54178Å), for Z =1. Least-squares refinement based on 7889 reflections with $I > 3.2\ \sigma(I)$ collected on a Enraf-Nonius CAD-4 diffractmeter and 968 parameters on convergence gave a final R of 0.059 and Rw of 0.052. GOF = 2.84. The structure were solved and refined using the TEXSAN Ver. 2.0 crystallographic program package of the Molecular Structure Corporation. Some non-hydrogen atoms were refined anisotropically. The absolute configulation was determined by anomalous scattering of Cu Kα radiation.

Crystal data for $[\mathbf{1}{\bullet}Cu(II)(hfac)_2]_n$: brown 0.20 × 0.10 × 0.10 mm^3; triclinic, space group $P\bar{1}$ (No. 1), with a = 11.2831(7) Å, b = 11.5615(7) Å, c = 18.0163(9) Å, α = 82.384(4)°, β = 74.242(4)°, γ = 61.826(5)°, V = 1993.9(2) $Å^3$, and D_X = 1.43 g/cm^3 for Z = 1. Least-squares refinement based

on 11531 reflections with $I > 2.0\,\sigma(I)$ collected on a Enraf-Nonius CAD-4 diffractmeter and 973 parameters on convergence gave a final R of 0.085 and Rw of 0.074. GOF = 5.2. The structure were solved and refined using the TEXSAN Ver. 2.0 crystallographic program package of the Molecular Structure Corporation. All non-hydrogen atoms were refined anisotropically.

RESULTS AND DISCUSSION

Structure of $\{1{\bullet}Mn(II)(hfac)_2\}_n$ and $\{1{\bullet}Cu(II)(hfac)_2\}_n$

The X-ray crystal structure analysis of $\{1{\bullet}M(II)(hfac)_2\}_n$ (M = Mn, Cu) revealed that the M(II) ions have an octahedral coordination environment with four oxygen atoms of two hfac anions and two oxygen atoms of two aminoxyl radicals. The M(II) ion in an octahedral position is attached to the two aminoxyl oxygens from two different biradical molecules in the *trans* disposition. The oxygen atoms of the terminal aminoxyl radicals of biradical **1** are ligated to two different M(II) ions to form a one-dimensional chain along the *c* crystal axis.(FIGURE 1) The bisaminoxylbenzene unit is in a chiral conformation and form a one-dimensional polymeric structure. Since the crystal has no symmetry element the molecule is fully chiral. The molecule not only contains a (*S*) chiral carbon center but also (*R*) C2 chiral skeleton of the organic ligand.

Magnetic properties

The temperature dependence of paramagnetic susceptibility of **1** was measured at 5000 Oe from 2 K to 250 K.(FIGURE 2.). The μ_B value of 2.61 μ_B at 250 K is close to a spin-only theoretical value of 2.83 μ_B for a triplet species. The magnetic data were analyzed by a Bleaney-Bowers type singlet-triplet model for the diradical with a weak intermolecular interaction, which is treated by the Weiss field, in which the magnetic exchange coupling constant J corresponds to a Heisenberg Hamiltonian $\boldsymbol{H} = -2JS_a{\bullet}S_b$ for the spins S_a and

$$\chi_m = \frac{2PNg^2\mu_B{}^2}{k_B(T-\theta)\{3+\exp(-2J/k_BT)\}} \qquad (1)$$

S_b in the diradical **1**.[12] The best fit parameters were $-2J/k_B = 461.8$ K, $\theta = -3.7$ K and $P = 91.3$ % in a temperature range of 9 - 245 K, where P is purity factor and other symbols have their usual meaning.

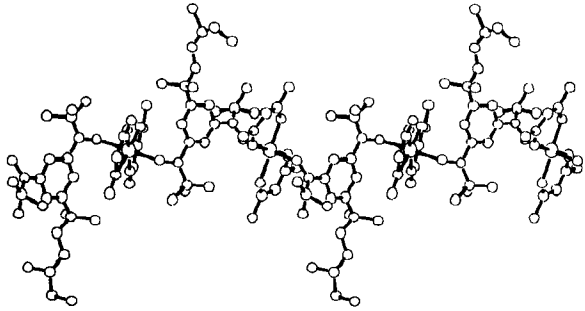


FIGURE 1 The X-ray crystal structure of the complex of [**1**•Mn(II)(hfac)$_2$]$_n$. Hydogen atoms and fluorine atoms are omitted for clarity.

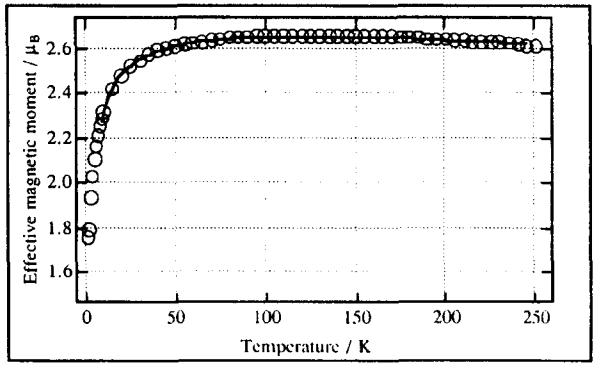


FIGURE 2. Observed effective magnetic moment vs. T plot for the diradical **1** measured in a magnetic field of 5000 Oe. Solid line is calculated by a Bleany-Bowers type model for the diradical **1**.

The temperature dependence of the magnetic susceptibility was investigated in 5000 Oe for the both Mn(II) and Cu(II) complexes. FIGURE 3 shows the temperature dependence of the magnetic susceptibility for

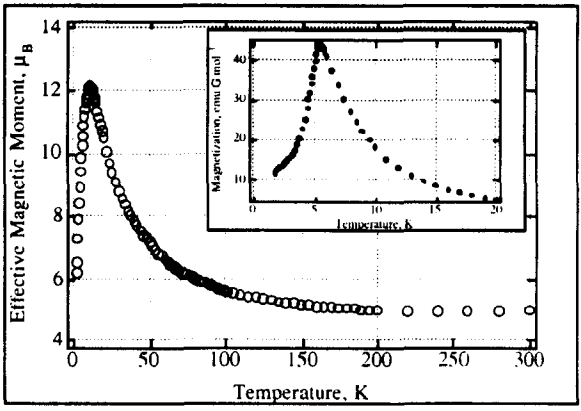


FIGURE 3 Temperature dependence of magnetic moment in 5000 Oe of a polycrystalline sample of [**1**•Mn(II)(hfac)2]n. Inset shows the temperature dependence of magnetization in 5 Oe of a polycrystalline sample.

{**1**•Mn(II)(hfac)2}n. The μ_{eff} value of 4.91 at 300 K is smaller than a theoretical value of 6.43 for paramagnetic spins of two 1/2 spins of organic radical and one 5/2 spins of d^5 Mn(II) and larger than 3.87 for antiparallel spins of two 1/2 spins of organic radicals and 5/2 spins of d^5 Mn(II). Together with a lack of a minimum at lower temperature, the room temperature μ_{eff} value suggest the occurrence of strong (more negative than -300 K) antiferromagnetic coupling between the aminoxyl radical as a ligand and Mn(II) ion. When the measurement was carried out in 5 Oe, the magnetic susceptibility showed a cusp at 5.4 K. (FIGURE 3 inset) The magnetization at 1.8 K revealed metamagnetic behavior (FIGURE 4). Namely, while the response of the magnetization was not sensitive to the weak applied magnetic field below ca. 500 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 4 (Inset)). A saturation magnetization value of ca. 2.7 μ_B was reached at 1.8 K at 3 Tesla. When the interaction between the manganese(II) ion and **1** is antiferromagnetic ($J_2 < 0$ in Scheme I), the value of [**1**•Mn(II)(hfac)2]n is expect to be 3 μ_B (5 / 2 - 2 / 2 = 3 / 2) in good agreement with the observed value. These magnetic behaviors

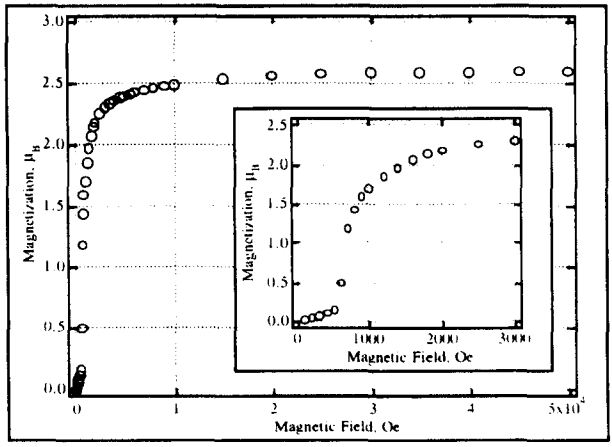


FIGURE 4 Field dependence of the magnetic moment at 1.8 K. Inset shows magnetic field range of 0 to 3000 Oe.

are similar to those found in Mn(II)(hfac)$_2$ complex with non-chiral biradical **1H** (R = H).[3]

The paramagnetic susceptibility of {**1**•Cu(II)(hfac)$_2$}$_n$ was also investigated in the temperature range 20 - 230 K. (FIGURE 5) The μ_{eff} value of 2.96 μ_B at 230 K agred well with the theoretical value of 3.0 μ_B for three

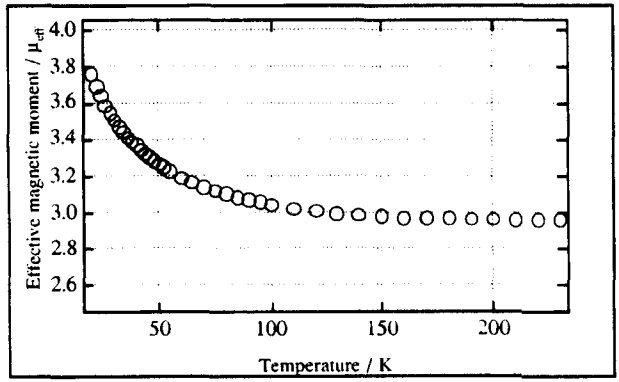


FIGURE 5 Temperature dependence of magnetic moment in 5000 Oe of a polycrystalline sample of [**1**•Cu(II)(hfac)$_2$]$_n$.

non-interacting paramagnetic 1/2 spins. The μ_{eff} value increased with decreasing temperature and showed the maximum at 4 K. This results indicate that the ferromagnetic interaction occur between the bisaminoxyl radical **1** and copper (II) ion. However, preliminary results of field dependence of magnetic susceptibility at 2 K is indicative of absence of long range ordering.

CONCLUSION

It is concluded that (*R*)-helical 1-D molecule-based metamagnet has been realized. (Scheme 1) It not only contains a (*S*) chiral carbon center but also (*R*) *C2* chiral skeleton of the organic ligand. The interaction between the 1-D chains is expected to be weakly antiferromagnetic, making the **1**•Mn(II)(hfac)$_2$ complex, an assembly of the 1-D chains, a molecular based metamagnet. The temperature dependence of the magnetization revealed that the heterospin system behaves as a metamagnet below 5.4 K. This material may be important in the experimental observation of MChD effect.

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