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[14] The required linear octapeptide [H(D-^{Me}*N*-Ala-L-(*p*-MeBlz)Cys-(D-^{Me}*N*-Ala-L-Phe)$_3$-COOH] was prepared by solid-phase methods and cleaved from the resin by basic hydrolysis. After cyclization in solution and removal of the cysteine protecting group, the resulting cyclic peptide was alkylated with 4,4′-(bromomethyl)azobenzene to give **1** after RP-HPLC purification. MS (ESI): m/z: 1977 [M+H$^+$], (calcd: 1976.9).

[15] For analytical investigations the peptide solutions in CH_2Cl_2 were dried over molecular sieves. After removal of the CH_2Cl_2 **1** was dissolved in $CHCl_3$ and $CDCl_3$ (previously dried over P_2O_5).

[16] Solutions of (*E*)-**1** in chloroform in daylight contain small amounts of (*Z*)-**1** (E:Z = 90:10, as determined by ^{1}H NMR spectroscopy).

[17] Irradiation at 366 nm was performed with a 4 W UV lamp. At a concentration of 0.05 mM the photostationary equilibrium was obtained after 5 min.

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[19] ^{1}H NMR spectroscopic data shows 4,4′-dimethylazobenzene, for example, has an E:Z ratio of 20:80 at the photostationary equilibrium (UV irradiation with 366 nm).

[20] Irradiation with visible light was performed with a 15 W fluorescence lamp (Philips F15T8/CW). At a concentration of 0.05 mM the photostationary equilibrium was obtained after 20 min.

[21] ^{1}H NMR data for (*Z*)-**1** (400 MHz, 293 K, ca. 3 mM in $CDCl_3$): L-Phe^1**:** 8.68 (d, J = 9.1 Hz, NH); 5.32 (m, CH); 2.88–3.04 (m, $C^{\beta}H_2$); 7.14–7.25 (m, $C^{\delta,\varepsilon,\xi}H$); D-^{Me}*N*-Ala^2: 2.79 (s, NCH_3); 5.85 (q, J = 6.5 Hz, C-H); 1.03 (d, J = 6.8 Hz, $C^{\beta}H_3$); L-Phe^3: 8.72 (d, J = 8.7 Hz, NH); 5.27 (m, $C^{\alpha}H$); 2.88–3.04 (m, $C^{\beta}H_2$); 7.14–7.25 (m, $C^{\delta,\varepsilon,\xi}H$); D-^{Me}*N*-Ala^4: 2.76 (s, NCH_3); 5.89 (overlap., $C^{\alpha}H$); 0.98 (d, J = 7.0 Hz, $C^{\beta}H_3$); L-Phe^5: 8.69 (d, J = 8.7 Hz, NH); 5.29 (m, $C^{\alpha}H$); 2.88–3.04 (m, $C^{\beta}H_2$); 7.14–7.25 (m, $C^{\delta,\varepsilon,\xi}H$); D-^{Me}*N*-Ala^6: 2.76 (s, NCH_3); 5.75 (q, J = 7.0 Hz, $C^{\alpha}H$); 0.92 (d, J = 7.0 Hz, $C^{\beta}H_3$); L-Cys^7: 8.41 (d, J = 8.6 Hz, NH); 5.19 (m, $C^{\alpha}H$); 2.67 (2.18, m, $C^{\beta}H_2$); 3.56 (br s, $SCH_2C_6H_4N{=}$); 7.07 (d, J = 8.1 Hz, $SCH_2C_6H_4N{=}$); 6.56 (d, J = 8.1 Hz, $SCH_2C_6H_4N{=}$); D-^{Me}*N*-Ala^8: 3.43 (s, NCH_3); 5.89 (overlap., $C^{\alpha}H$); 1.23 (d, J = 7.0 Hz, $C^{\beta}H_3$).

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[23] ^{1}H NMR data of (*E*)-**1** (500 MHz, 293 K, ca. 3 mM in $CDCl_3$): δ = 8.42–8.81 (m, NH of L-Phe and L-Cys in H bond); 7.70–7.85 (m, L-Cys $SCH_2C_6H_4N{=}$); 7.32–7.50 (m, L-Cys $SCH_2C_6H_4N{=}$); 7.14–7.24 (m, L-Phe $C^{\delta,\varepsilon,\xi}H$); 7.08–7.15 (m, free NH of L-Phe and L-Cys); 4.57–5.92 (m, L-Phe, L-Cys, and D-^{Me}*N*-Ala $C^{\alpha}H$); 2.52–3.80 (m, L-Phe, L-Cys $C^{\beta}H_2$, L-Cys $SCH_2C_6H_4N{=}$, D-Me*N*-Ala NCH_3); 0.84–1.28 (m, D-Me*N*-Ala $C^{\beta H3)}$.

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A Chiral Molecular Based Metamagnet Prepared from Manganese Ions and a Chiral Triplet Organic Radical as a Bridging Ligand[**]

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The design of molecular materials with interesting optical and/or magnetic properties has been one of the major challenges of the last few years.[1, 2] In 1984 Barron and Vrbancich gave the name "magneto-chiral dichroism" (MChD) to the relationship between natural optical activity and magnetic field induced circular dichroism.[3] In 1997 Rikken and Raupach observed the MChD effect for tris-(3-trifluoroacetyl-(±)-camphorato)europium(III) in the paramagnetic state.[4] The MChD effect depends on the magnitude of the magnetic moment. It is important to make fully chiral molecule-based magnets, which are expected to exhibit a strong MChD effect. Although novel properties are expected for such compounds, there are only a few examples of molecule-based chiral magnetic material.[1, 5–7]

Recently, a strategy of using π-conjugated polynitroxide radicals with high-spin ground states as bridging ligands for magnetic metal ions was applied to assemble and align electron spins on a macroscopic scale.[8–11] The crystal structures and the magnetic structures of these complexes

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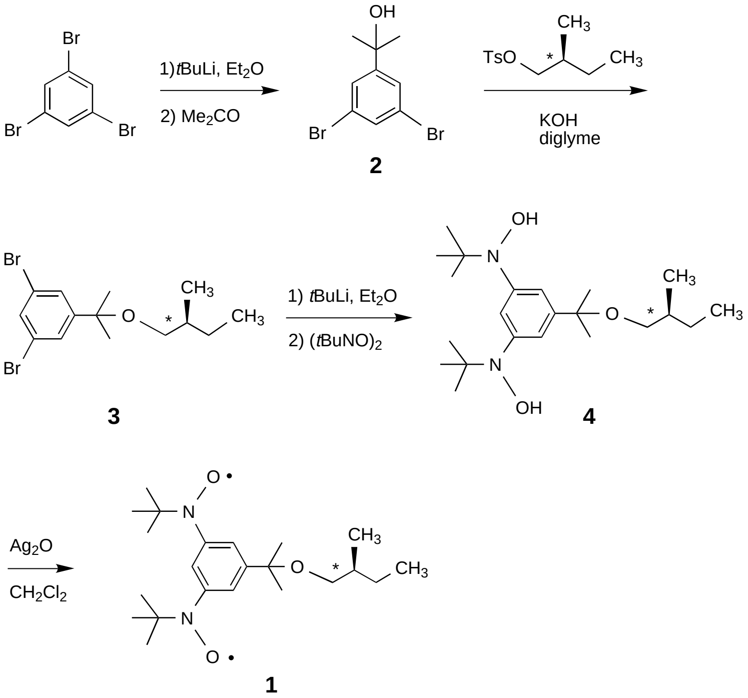
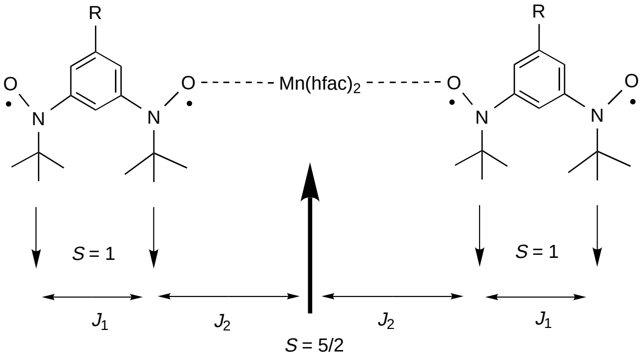
are known. The dimensionality of the complex as well as the sign and magnitude of the exchange coupling between neighboring spins can be readily tuned by this strategy.[12] We are able to synthesize one-dimensional complexes by using bis-monodentate bisaminoxyl radicals as bridging ligands and manganese(II) hexafluoroacetylacetonate ($[Mn^{II}(hfac)_2]$; Scheme 1).[8, 9] The biradical **A** (R = H, Scheme 1) has been established to have a triplet ground state with a large intramolecular ferromagnetic coupling of $J_1/k_B > 300$ K,[13] where J_1 is defined as an intramolecular exchange parameter in the Heisenberg Hamiltonian $\boldsymbol{H} = -2J_1\boldsymbol{S}_a \cdot \boldsymbol{S}_b$ for the spins $\boldsymbol{S}_a$ and $\boldsymbol{S}_b$ in the same molecule of **A** (R = H). In the complex, two *tert*-butylaminoxyl groups are rotated out of the plane of the phenylene ring in a conrotatory manner; each molecule **A** (R = H) in the crystal has no symmetry element and is therefore chiral (that is, *R*- or *S*-configured). The one-dimensional polymeric chains are isotactic, as all units are of the same chirality. The crystal lattice as a whole is achiral because enantiomeric chains are present.[8–11] Here we report the synthesis, structure, and magnetic properties of a novel chiral heterospin system which behaves as a metamagnet below 5.4 K.



Scheme 2. Synthesis of **1**.



Scheme 1. Schematic representation of the one-dimensional chain formed by Mn^{II} ions and bridging biradicals **A**, which are ferromagnetically coupled.

The chiral biradical **1** was prepared according to Scheme 2. It was mixed with an equimolar amount of dehydrated $[Mn(hfac)_2]$ in diethyl ether/*n*-heptane, and the mixture was concentrated. Deep brown block crystals were obtained upon storage for one day at $-30\,^{\circ}C$.

An X-ray crystal structure analysis of a triclinic crystal of the complex revealed the formation of a one-dimensional, helical structure (Figure 1).[14] The oxygen atoms of the aminoxyl moieties of **1** are ligated to two different manganese ions to form a one-dimensional helical chain along the *c* crystal axis. Each manganese ion has an octahedral coordination sphere in which the aminoxyl oxygen atoms from two different biradical molecules are in *trans* sites. The bisaminoxylbenzene unit is in a chiral conformation and forms a protein α-helix-type *R*-helical structure.

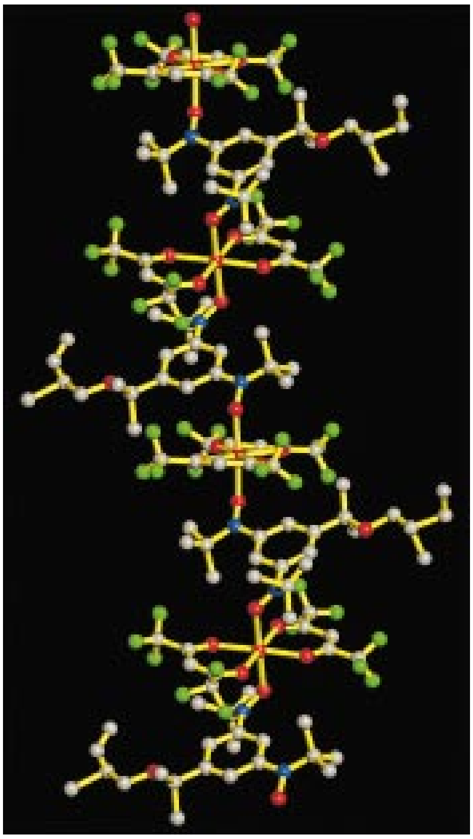


Figure 1. X-ray crystal structure of $[\mathbf{1} \cdot Mn^{II}(hfac)_2]_n$. The hydrogen atoms are omitted for clarity. Gray: carbon, blue: nitrogen, red: oxygen and manganese, green: fluorine.

The UV/Vis spectra of the complex $[\mathbf{1} \cdot Mn^{II}(hfac)_2]_n$ were measured in solution (hexane) and in the crystalline state (KBr disk). Both spectra exhibit absorptions around 300 nm and 455 nm, and are very similar to each other and different from that of **1**. Therefore it is reasonable to consider that the complex retains the interaction between units of **1** and $Mn^{II}(hfac)_2$ in hexane. The solution of $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ in hexane exhibits an optical rotation of $[\alpha]^{25}_{589} = -314$ ($c = 0.00635$ in hexane)), which is an indication that $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ is chiral in solution.

The temperature dependence of the magnetic susceptibility of $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ was investigated in a magnetic field of 5000 Oe. The μ_{eff} value of 4.91 μ_B at 300 K is smaller than the theoretical value of 6.43 μ_B for paramagnetic isolated spins of two 1/2 spins of organic radical and one 5/2 spin of d^5 Mn^{II} and larger than the value of 3.87 μ_B for two 1/2 spins of organic radicals and 5/2 spins of d^5 Mn^{II} in antiferromagnetic coupling. Together with the lack of a minimum at lower temperature, the room-temperature μ_{eff} value suggests the occurrence of strong ($J_{NO-Mn}/k_B < -300$ K) antiferromagnetic coupling between the Mn^{II} ions and the aminoxyl radical ligands. When the measurement was carried out in a magnetic field of 5 Oe, the magnetic susceptibility showed a cusp at 5.4 K. The magnetization at 1.8 K revealed metamagnetic behavior (Figure 2); the response of $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ to the magnetization was not sensitive to the weak applied magnetic field below about 500 Oe; this behavior is characteristic of an antiferromagnet. A sharp rise in magnetization and an approach to saturation, which is characteristic of a ferromagnet, was observed at higher applied magnetic field (inset of Figure 2). A saturation magnetization value of about 2.7 μ_B was reached at 1.8 K and 3 T. When the interaction between the manganese(II) ion and **1** is antiferromagnetic ($J_2 < 0$ in Scheme 1), the magnetic susceptibility of $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ is expected to be 3 μ_B ($5/2 - 2/2 = 3/2$), which is in good agreement with the observed value. This magnetic behavior is similar to that observed for a $Mn^{II}(hfac)_2$ complex with a nonchiral biradical.[9]

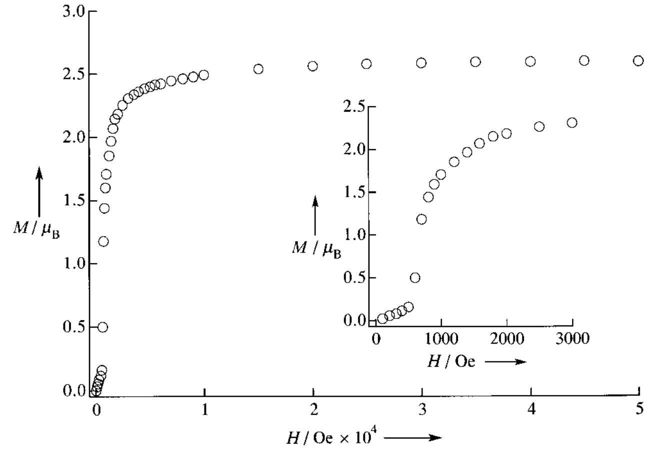


Figure 2. Dependency of the magnetic moment of a polycrystalline sample of $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ on the applied field at 1.8 K. Inset: enlargement for the applied magnetic field range 0–3000 Oe.

It is concluded that with $[\mathbf{1}\cdot Mn^{II}(hfac)_2]_n$ a *R*-helical, one-dimensional, molecule-based metamagnet has been prepared. It not only contains an *S*-configured chiral carbon center, but also an *R*-configured C_2 chiral skeleton of the organic ligand. The interaction between the manganese ions and the bisaminoxyl radical ligands is expected to be strongly antiferromagnetic. The temperature dependence of the magnetization and the magnetization curve revealed that the heterospin system behaves as a metamagnet below 5.4 K. Attempts to measure the MChD effect for this complex are in progress.

Experimental Section

4: Compound **3**[15] was treated by *tert*-butyllithium, and the mixture was stirred for 1 h. Nitroso-*tert*-butane was added to give **4** as a white powder; m.p. 169.8–170.2 °C (decomp.). MS: *m/z*: 380; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.40$ (brs, 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).

1: Compound **4** was oxidized with silver oxide in dichloromethane at 0 °C. The resulting product was purified by column chromatography on silica gel eluted with dichloromethane and then ditheyl ether. MS: *m/z*: 378; HR-MS: *m/z* calcd. for $C_{22}N_2O_3H_{38}$: 378.2882, found: 378.2869; EPR (9.4507 GHz, CH_2Cl_2, room temperature): $g = 2.0055$, $a_N = 13.1$ G; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 285 nm (20200); $[\alpha]^{25}_{436} = -1026$ ($c = 0.02775$ in hexane).

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