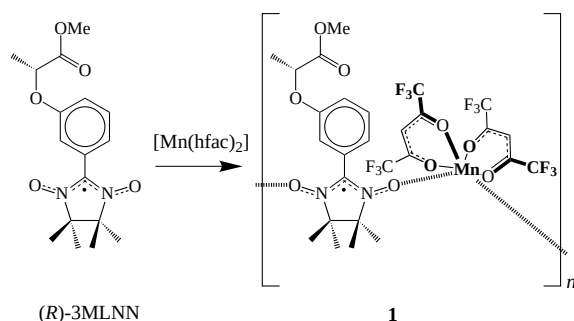


An Enantiopure Molecular Ferromagnet**

Maria Minguet, Dominique Luneau,* Elsa Lhotel, Vincent Villar, Carley Paulsen, David B. Amabilino, and Jaume Veciana*

The importance that the presence of chirality—resulting from the presence of atomic stereogenic centers or atropisomeric conformations—may have in the behavior of molecular magnetic materials is an open question of great current interest.^[1] This interest has been encouraged by the observation of magneto–chiral effects,^[2] although other upshots of chirality as a result of symmetry breaking may be possible.

In an effort to unveil some of these possible influences, we initially focused on the synthesis of purely organic chiral α -nitronyl nitroxides,^[3] of which (*R*)-3MLNN (Scheme 1) is one.^[4] Here, we report the preparation and optical and magnetic properties of the coordination compound **1**, comprised of this radical and manganese(II) bis(hexafluoroacetylacetonate) ($[\text{Mn}(\text{hfac})_2]$).



Scheme 1. Preparation of the complex **1**.

We were drawn to metallo–organic molecular magnetic materials^[5] because of: 1) their relatively high magnetic ordering temperatures compared with their organic counterparts,^[6] 2) their rich variety of chiral coordination modes,^[7] and 3) the anisotropy of the magnetic moments associated with the metal ions that could favor the observation of magneto–optical effects.^[2] The $\text{Mn}(\text{hfac})_2$ nitronyl nitroxide

complexes are known in a variety of guises^[8] which include helical chains in a complex which crystallizes in a chiral space group, with spontaneous resolution of enantiomorphic crystals, and magnetic ordering.^[9] In addition, complexation of the same metal complex by a chiral bisnitroxide led to the formation of a metamagnet.^[10] The crystalline enantiopure chiral complex **1** reported here has homochirality as well as a ferromagnetic phase transition at 3 K. Below the transition temperature, intriguing dynamic behavior is observed culminating in the opening up of hysteresis loops below 800 mK. An explanation of this phenomenon is domain-wall pinning and depinning. Another interesting result is the observation of a magnetic avalanche phenomenon below 0.3 K.

The crystalline complex **1** (Scheme 1) exists as a coordination polymer in which each oxygen atom of the ONCNO unit of the radical coordinates to the paramagnetic metal ion in a *cis* manner (Figure 1a). The metal ion centers have the *A* configuration, or minus (*M*) helicity. The molecular conformation of the radical component in the complex is remarkably similar to the pseudo-eclipsed one present in crystals of the pure organic ligand, which crystallizes in the same chiral space group ($P2_12_12_1$).^[11] The polymeric chains run along the *b* axis (Figures 1b and 1c), with a distance

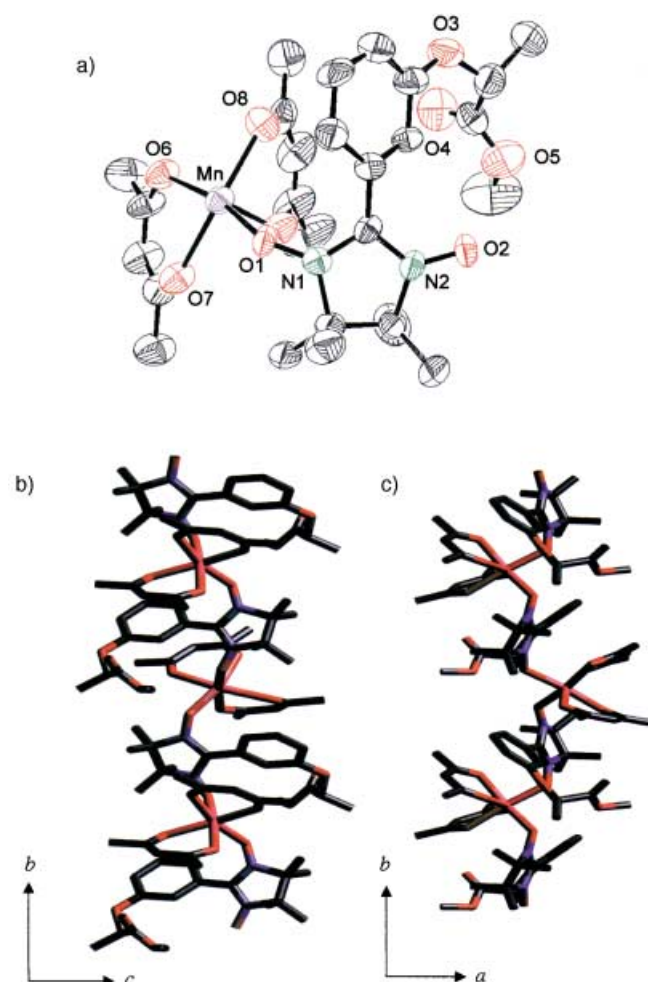


Figure 1. The crystal structure of **1**: a) An ORTEP view^[15] of the monomeric unit; cylindrical representations of b) the homochiral chains in the *a* plane and c) in the *c* plane (hydrogen and fluorine atoms omitted for clarity).

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between Mn^{II} ions within the chains of 7.57 Å. There are very short distances (3.30 and 3.43 Å) between the phenyl rings of the radical ligand and the CO group of the hfac ligands, consistent with π - π interactions, which may play an important role in determining the structure of the polymeric chain.^[9] The chains pack in a parallel manner such that each one is surrounded by six neighboring chains some of which are related by a screw-axis. The shortest inter-chain distances are between fluorine atoms of the CF_3 groups and CH groups from the two ligands (the six closest metal ion to metal ion distances are in the range 11.33–12.54 Å).

The UV/Vis absorption spectra of the complex **1**, recorded in KBr matrix, shows a longer wavelength visible absorption than the pure radical. This shift in the absorption is mirrored by changes in the optical activity of the complex, which was confirmed by performing circular dichroism (CD) spectroscopy of the ground crystals, also in KBr matrix (Figure 2).^[11] The Cotton effects displayed by the complex are as intense as those of the radical except for that at the longest wavelength. The significant positive effect at approximately 460 nm is particularly interesting for the possible observation of magneto-chiral effects, given the higher natural CD asymmetry factor ($g_{\text{NCD}} = 2(\epsilon_- - \epsilon_+)/(\epsilon_- + \epsilon_+) = \Delta\epsilon/\epsilon$) than the ligand.

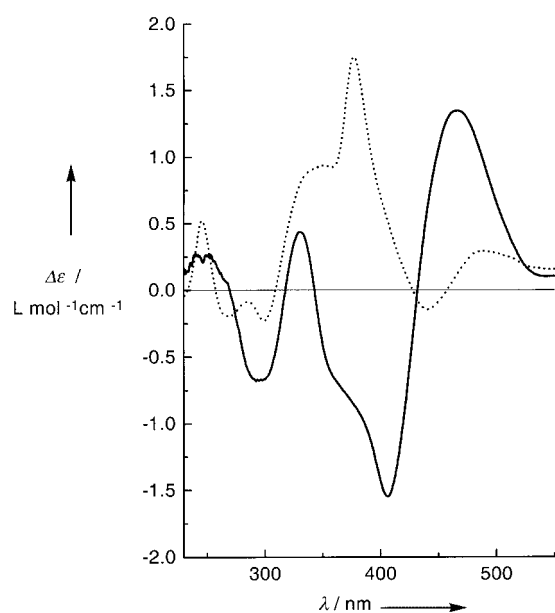


Figure 2. Solid state CD spectra of (R)-3MLNN (••••) and (R)-**1** (—) in KBr.

The temperature dependence of the molar magnetic susceptibility χ_m of a ground crystalline sample of **1** (measured in the temperature range from 2 to 350 K, Figure 3) shows a continuous increase of $\chi_m T$ upon cooling down to 3 K, from a value $\chi_m T = 5.6 \text{ cm}^3 \text{ K mol}^{-1}$ at 350 K, to very high values at low temperatures. Moreover, $\chi_m T$ shows a maximum at approximately 3 K, and decreases at lower temperatures. The increase of $\chi_m T$ upon cooling is the typical behavior of polymeric $\text{Mn}(\text{hfac})_2$ nitronyl nitroxide complexes, which behave normally as one-dimensional (1D) Heisenberg ferromagnets, in which the non-compensation of the isotropic spins of the Mn^{II} ion ($S = 5/2$) and of the radical ($S = 1/2$) leads to an

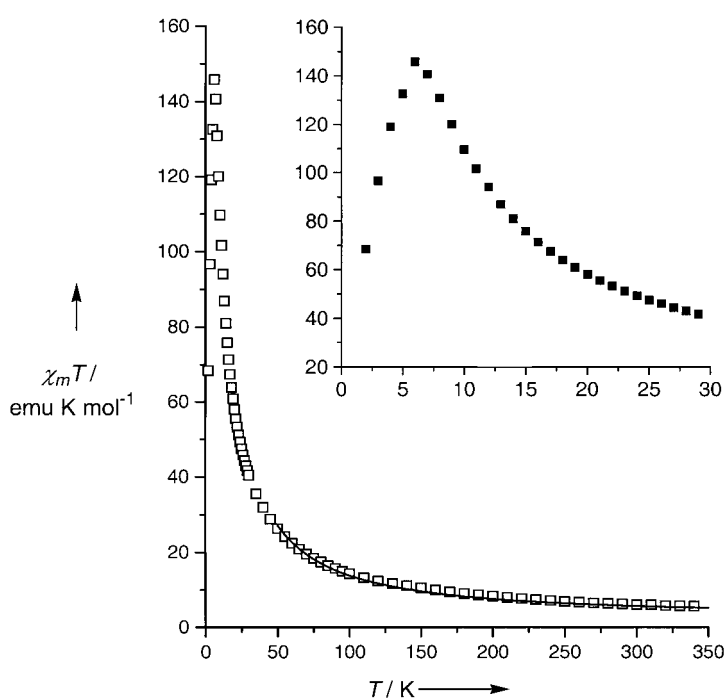


Figure 3. Temperature dependence of $\chi_m T$ versus T for a ground crystalline sample of (R)-**1**. The measurements were taken in a field of 100 Oe. The continuous line is the fit of experimental data ($\square$) above 50 K to the Seiden model. Inset: Expansion of the low-temperature region showing the maximum in $\chi_m T$.

increasing magnetic moment as the correlation length increases upon lowering the temperature. Fitting of the experimental data above 50 K to the Seiden model^[12] gives a J value (exchange coupling between $S = 1/2$ and $S = 5/2$ units) of -105 cm^{-1} with a fixed $g = 2$ value ($H = -2JS_1S_2$). This value is in the range of previous ones found in this type of $\text{Mn}(\text{hfac})_2$ nitronyl nitroxide complex.^[8,9] The presence of a maximum of $\chi_m T$ at low temperatures suggests that the already correlated spins within each chain order magnetically between the chains.

To investigate the possibility of a phase transition near 3 K, low-temperature alternating current (ac) susceptibility and direct current (dc) magnetization measurements were made using the low-temperature high-field superconducting quantum interference device (SQUID) magnetometer developed at the CRTBT/CNRS in Grenoble. Figure 4 shows ac susceptibility data as well as the zero-field cooled (ZFC) and field cooled (FC) dc susceptibility. The peak in the real part (χ') of the ac susceptibility at a Curie temperature (T_c) of 3 K, along with a small frequency-independent signal in the imaginary part (χ'') of the ac susceptibility is the signature of a ferromagnetic phase transition and the onset of three-dimensional (3D) long-range magnetic order. The very large value of the susceptibility $\chi' = 1.0 \text{ emu cm}^{-3}$ at the peak corresponds to a demagnetization factor of $1/\chi' = N = 1$, a reasonable value for the elongated shape of the sample. At temperatures between 30 K to approximately 6 K the susceptibility data can be reasonably well fit to the formula $\chi = (C/T)\exp(2J/kT)$ which is predicted for a 1D Ising spin chain and implies $T_c = 0$. Note that the use of this formula is justified by the presence of a uni-axial anisotropy observed at low temperature (see

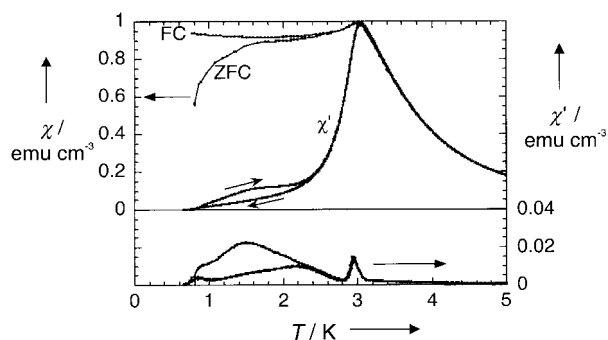


Figure 4. The real (χ') and imaginary (χ'') part of the ac susceptibility measured at 2.1 Hz in an ac field strength of approximately 0.1 Oe (bottom) and the zero-field cooled and field cooled dc susceptibility measured in a field of approximately 1 Oe (top). The measurements were made on an oriented small ($4 \times 0.9 \times 0.4$ mm) single crystal of mass 1.08 mg with the field aligned along the b axis (long direction) of the sample.

below). Near 6 K there is a crossover from the high-temperature 1D short-range correlations to 3D long-range ordering at T_c . Indeed after corrections for demagnetization effects the data can be scaled from approximately 5.5 K to T_c as $\chi = (T - T_c)^{-\gamma}$, and we find a value for the critical exponent $\gamma \approx 1.4$.

Below T_c nontrivial dynamic effects are observed. In particular from just below T_c to approximately 1 K, the ac susceptibility is highly nonlinear, depends strongly on the presence of (small) superimposed dc fields, is hysteretic in temperature, and above all is frequency dependent. Between approximately 1 and 0.6 K, χ' falls to zero, and a small but easily identifiable peak in χ'' is observed. Figure 5 shows the frequency dependence of the position of this peak, a straight line on this plot corresponds to a simple thermal activation law $\tau = \tau_0 \exp(E_b/k_B T)$ with $\tau_0 \approx 6 \times 10^{-11}$ s and where $E_b \approx 16$ K is an average activation energy barrier.^[13]

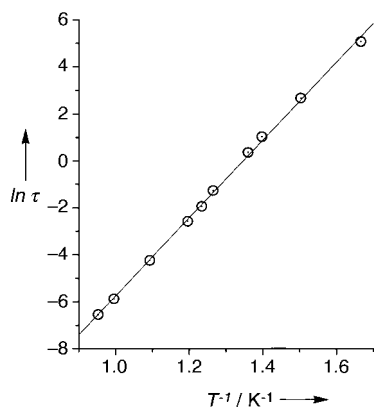


Figure 5. The frequency (f) dependence of the peak position in χ'' (observed near 1 K) for 0.001 to 180 Hz plotted as $\ln \tau$ versus $1/T$ where $\tau = 1/2\pi f$.

Associated with the increase in relaxation times as the temperature decreases and the abrupt decrease in χ'' below 1 K are the opening up of hysteresis loops (Figure 6). These data have been taken with a field step of 10 Oe, and with three measurements at each field. There is a small relaxation of the magnetization during the measurement of the hysteresis. Note that at 135 mK, the width of the loop is smaller than at

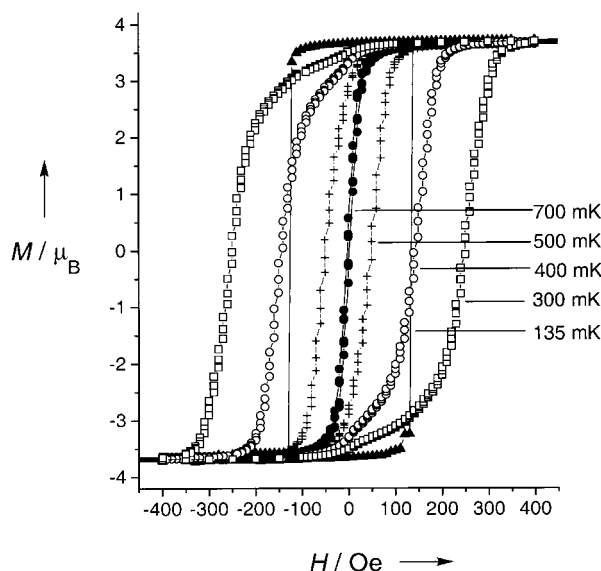


Figure 6. Opening up of hysteresis loops below 1 K showing the magnetic avalanche phenomenon.

300 mK! At this temperature, an avalanche of the magnetization is observed similar to those reported for the molecular cluster system $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]$.^[14] At a certain value of applied field, there is an abrupt switching of a population ΔM of spins (i.e. as a result of domain wall depinning), which releases an energy $2\Delta M B_{\text{int}}$ as local heating (B_{int} is the internal field). This heat in turn helps push more spins over the top of the thermal activation barrier, which creates more heat and so on resulting in the magnetic equivalent of an avalanche. Indeed, a temperature pulse is observed just after the avalanche.

At fields greater than approximately 1 Tesla the magnetization eventually saturates at a value of $4\mu_B$, which corresponds to an $S = 2$ spin ground state for the Mn^{II} radical unit. This result therefore confirms the strong antiferromagnetic coupling of the manganese(II) ions ($S = 5/2$) with the radicals ($S = 1/2$) along the chain. Finally, low-temperature magnetization measurements along the a and c axis were also made. M versus H for these directions indicate the existence of a relatively strong uni-axial anisotropy, with the easy axis (the direction along which the spins orient preferentially) aligned along the spin chain (b axis) direction. Such results were independently confirmed by oriented single-crystal ESR experiments at low temperatures.

The unusual dynamic behavior can be explained in terms of simple domain-wall motion. At T_c , domains are created with perhaps a long-laminar form along the easy axis of the crystal. Near T_c the walls are soft, and the energy is high enough so that the walls can be displaced easily, and thus the ac susceptibility remains large. As the temperature decreases, the domain walls become more rigid, and their displacement becomes increasingly hindered by defaults or pinning on the surface with characteristic energy of the order 16 K. Below 1 K, relaxation by thermal activation becomes very slow, and hysteresis loops can be measured, and as a result, the ac susceptibility decreases to near zero. The unusual dynamic effects, as well as the existence of the uni-axial magnetic

anisotropy, may be a result of the special asymmetry of this enantiopure molecular magnet. We are presently performing experiments to probe the origin of such results as well as investigating the magneto-optic properties of this intriguing material.

Experimental Section

1: (*R*)-Methyl[3-(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide) phenoxy]-2-propionate ((*R*)-3MLNN (50 mg, 0.15 mmol), ref.[4]) in CH₂Cl₂ (20 mL) was added to a warm heptane (20 mL) solution of manganese(II) bis(hexafluoroacetylacetonate) (70 mg, 0.15 mmol) and the mixture was allowed to cool to room temperature. Upon standing green needles of **1** (55 mg, 45%) crystallized. The complex gave satisfactory elemental, mass spectrometry, and IR spectroscopic analysis. Crystal data for **1** C₂₇H₂₅F₁₂MnN₂O₉, *M* = 804.43, orthorhombic, space group *P*2₁2₁2₁, *a* = 12.022(4), *b* = 14.219(5), *c* = 20.294(7) Å, *α* = *β* = *γ* = 90°, *U* = 3469.2(19) Å³, *Z* = 4, *ρ* = 1.540 g cm⁻³, *μ* = 0.495 cm⁻¹, *F*(000) = 1624, 3994 measured reflections, 2981 unique reflections, collected on a Bruker P4 diffractometer with monochromatic MoK_α radiation (*λ* = 0.71073 Å). Number of parameters 460 for 3994 independent reflections with *I* > 2σ(*I*); solution SHELXS-97 (Sheldrick, 1990), refinement SHELXL-97 (Sheldrick, 1997), final *R* indices [*I* > 2σ(*I*)] *R* = 0.0801, *R*_w = 0.1941. Weighted *R*-factors *R*_w and all goodness-of-fit *S* are based on *F*². CCDC-158455 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetic measurements were performed on crystalline samples of the complex. The temperature dependence of the magnetic susceptibility in the range 2–350 K was measured in a field of 500 G using a Quantum Design SQUID magnetometer. The low-temperature measurements below 7 K were made using a high-field SQUID magnetometer developed at CRTBT/CNRS.

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The First Polymer-Supported and Recyclable Chiral Catalyst for Enantioselective Olefin Metathesis**

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The rise of catalytic olefin metathesis as a practical and reliable method for efficient C–C bond formation has had a remarkable impact on organic and polymer synthesis.^[1] Ring-closing (RCM), ring-opening (ROM), and cross metathesis (CM) reactions have been developed in various laboratories

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