Chiral Ferrimagnetism

Structure and Magnetic Properties of a Chiral Two-Dimensional Ferrimagnet with T_C of 38 K**

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The construction of molecule-based magnetic materials, which possess additional properties such as conductivity,[1] photoreactivity,[2] or optical properties,[3–5] is currently a

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challenging target. Specific goals aimed for the latter two molecule-based magnets include: 1) The ability to design the molecular building blocks and to organize them in the solid for desired dimensionality, and 2) optical transparency.[3] The physical aspects of the current interest is centered on optical properties, particularly with respect to optical activity. When a magnet is characterized by optical transparency and chiral structure, there is a great possibility that the crystals have a chiral spin structure. These magnets display asymmetric magnetic anisotropy and magnetochiral dichroism.[4] This category of materials is not only of academic interest; they also afford the potential of being used in new devices. When chiral molecule-based magnets are constructed, chirality must be controlled in the molecular structure as well as in the entire crystal structure. As a consequence of this difficulty, only few examples of this type of magnet exist. Until now, most of the reported chiral magnets have low-dimensional magnetic structures, in which the magnetic ordering temperatures are below 10 K.[5] To afford a high-T_C magnet, dimensionality of the magnetic structure must be extended. When magnetic building blocks with more than three connections are introduced, two or three-dimensional magnets might be prepared. In 2001, we reported a three-dimensional (3D) chiral complex that was prepared by using this strategy.[8] Here we report on the crystal structure and optical and magnetic properties of a new 2D chiral ferrimagnet; $[\{Cr(CN)_6\}\{Mn(S)\text{-}pnH(H_2O)\}](H_2O)$ (**1**); ((*S*)-pn = (*S*)-1,2-diaminopropane).

The complex **1**[6] was obtained as green needle-shaped crystals by the reaction of a solution of $K_3[Cr(CN)_6]$, $Mn(ClO_4)_2$, and (*S*)-1,2-diaminopropane dihydrochloride ((*S*)-pn·2 HCl) in a 1:1:1 molar ratio in methanol/H_2O (1:1), adjusted to pH 6–7 with KOH under an argon atmosphere. X-ray structural analysis found an orthorhombic unit cell and the structure revealed the formation of a two-dimensional chiral network (Figure 1).[7] Four cyanide groups in the $[Cr(CN)_6]^{3-}$ ion are ligated to Mn^{2+} ions to form a bimetallic square, which is arranged almost perpendicular to the *c* axis. Each unit has one chiral (*S*)-pn ligand and two water molecules between the sheets. The (*S*)-pn ligand and one of the water molecules coordinates to an Mn^{2+} ion and separates the sheets. The two shortest intersheet metal separations are observed between the Mn and Cr atoms (7.3105(4) and 7.7701(4) Å, respectively), which describe a ferromagnetic interaction between 2D sheets from the point of view of a magnetic dipole interaction, while the shortest intersheet homometallic contacts are greater than 8 Å.

The magnetic behavior of the complex was measured using a SQUID magnetometer. The temperature dependence of $\chi_{mol}T$ values are displayed in Figure 2. The $\chi_{mol}T$ value is 5.01 emu K mol^{-1} (6.33 μ_B) at 300 K, and decreases with decreasing temperature down to a minimum value of 3.65 emu K mol^{-1} (5.41 μ_B) at 85 K. The extrapolated value of the effective magnetic moment (7.07 μ_B) is in good agreement with the spin-only theoretical value. (Figure 2; inset: Paramagnetic spin of $5/2 + 3/2 \rightarrow 7.07\ \mu_B$) Upon further cooling, the $\chi_{mol}T$ value increases and diverges. In both the field-cooled (FC) and zero-field-cooled (ZFC) cycles, and with a low applied field (5 Oe) in the temperature range of 5–100 K, a long-range magnetic ordering is observed below 38 K (Figure 3). As shown in Figure 4, the magnetization (*M*) increases sharply with applied field and is saturated rapidly.

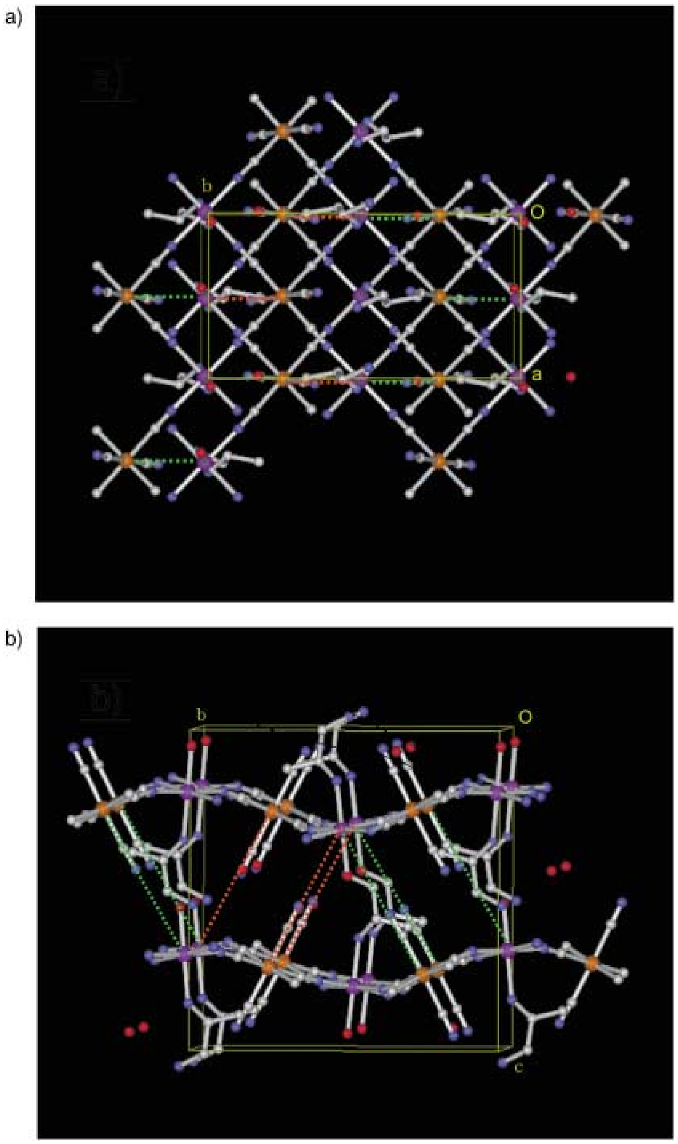

Figure 1. X-ray crystal structure of **1**. Atoms: Mn (purple), Cr (orange), N (blue), and C (gray).

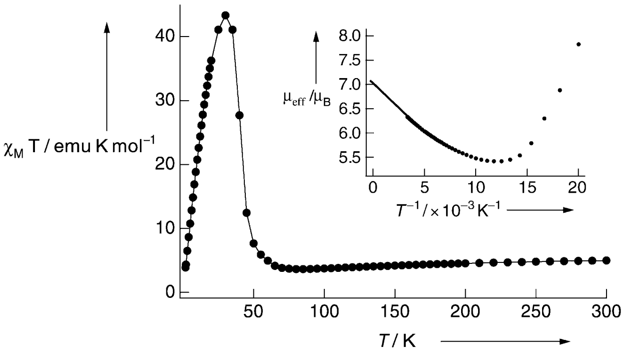

Figure 2. Temperature dependence of $\chi_{mol}T$ for **1**. Inset: Plot of μ_{eff} versus T^{-1}.

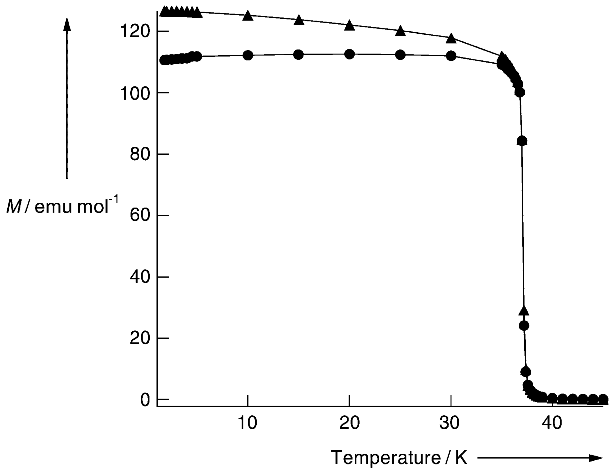

Figure 3. Temperature dependence of magnetization for a polycrystalline sample of **1** at 5 Oe: Zero-field-cooled (ZFC, ●) and field-cooled magnetization (FC, ▲).

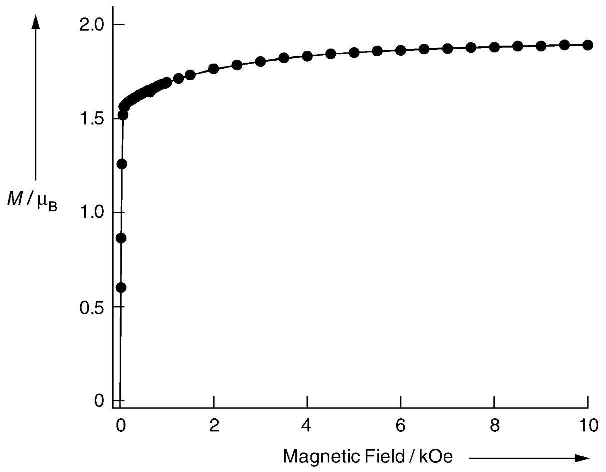

Figure 4. Field dependence of the magnetization of a polycrystalline sample of **1** at 5 K.

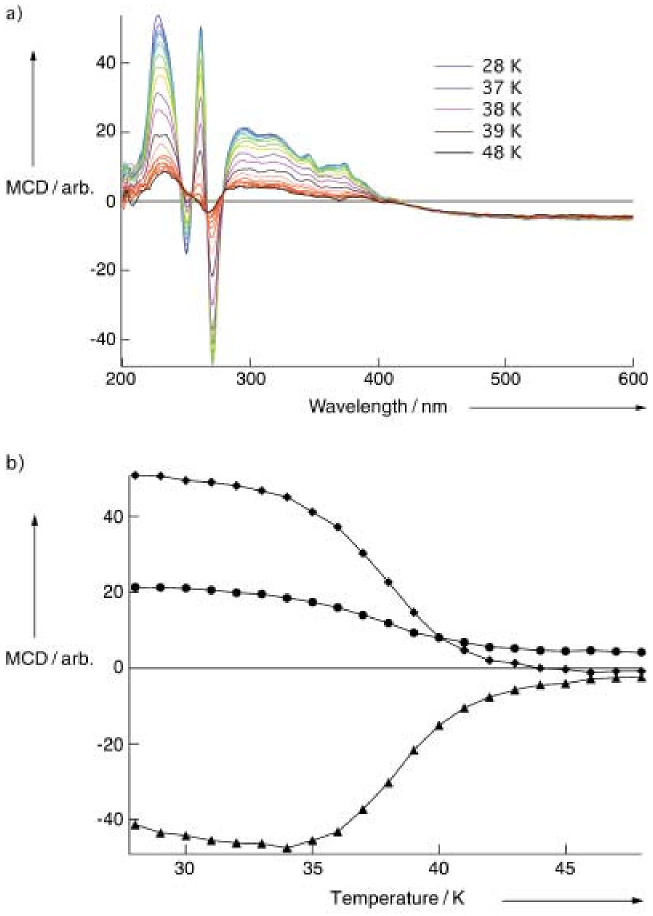

Figure 5. a) Temperature-dependent (28–48 K) MCD spectra of **1** (KBr disk) at 1 kOe; b) Temperature dependence of the MCD intensity at 295 (●), 270 ▲, and 261 nm ◆.

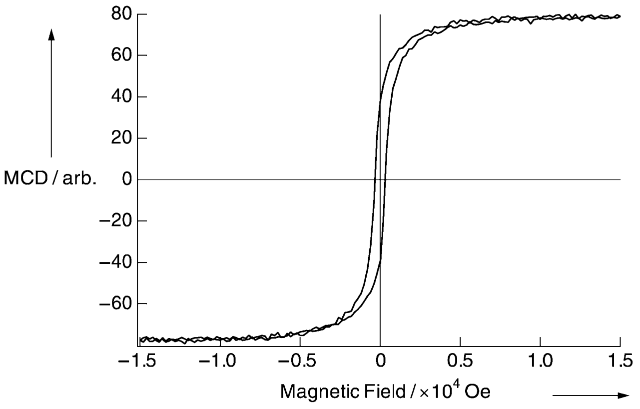

Figure 6. Field dependence of the MCD intensity at 6 K.

The saturation magnetization is $M_S = 2\,\mu_B$. This value is in good agreement with the theoretical value of antiferromagnetic coupling between Cr^{3+} and Mn^{2+} ions. ($5/2-3/2=1$) A hysteresis loop (with a remnant magnetization of 1800 emu G mol^{-1} and a coercive field of 10 Oe) was observed at 5 K, which suggests a soft magnetic behavior.

(Magnetic) circular dichroism ((M)CD) spectra of complex **1** were measured within a pressed KBr disk in a magnetic field of 0–10 kOe, and in the temperature range of 10–300 K. The temperature dependence of the MCD spectra at 10 kOe is shown in Figure 5. The MCD spectra enhanced at around the critical temperature T_C.(Figure 5B) This behavior originates from Faraday effect that is exhibited by this material. The field dependence of the MCD spectra at 6 K is shown in Figure 6; hysteresis is observed at this temperature.

In summary, we have successfully constructed and structurally characterized the first two-dimensional, fully chiral ferrimagnet. Furthermore, the magnetic transition temperature of this complex is relatively high (38 K) among the known molecule-based magnets. We believe that this complex is a potential candidate for novel magneto-optical phenomena. In the future, these complexes should lead to the development of a novel group of molecule-based magnetic materials.

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[6] IR in KBr (Supporting Information): $\tilde{\nu}_{CN} = 2157.0$ (Cr-CN-Mn), 2137.7 cm^{-1} (Cr−CN, terminal).

[7] Crystal data for $[\{Cr(CN)_6\}\{Mn(S)\text{-pnH}(H_2O)\}](H_2O)$: green needle, $C_9H_{14}CrMnN_8O_2$, $M_r = 374.22$, orthorhombic, space group $P2_12_12_1$, $a = 7.6280(17)$, $b = 14.510(3)$, $c = 14.935(3)$ Å, $V = 1653.1(6)$ Å^3, $Z = 4$, crystal size $0.2 \times 0.05 \times 0.05$ mm^3, $\mu(Mo_{K\alpha}) = 1.436$ mm^{-1}. Data were collected with a Bruker SMART-APEX three-circle diffractometer, equipped with a CCD area detector (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, ω-scan mode (0.3° steps), semi-empirical absorption correction on Laue equivalents). The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data using SHELXTL software. Hydrogen atoms were included in calculated positions but not refined. All non-H atoms were refined anisotropically. The refinement converges with $R_1 = 0.0265$ for 2377 data $(I > 2\sigma(I))$, $wR_2 = 0.0709$ for 2383 unique data $(2.73 \geq \theta \geq 23.28°)$, Flack parameter = 0.01(3), max/min residual electron density 0.108/−0.683 e Å^3. CCDC-172588 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).

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