Inorg. Chem. **2002**, *41*, 4615–4617

Inorganic Chemistry
Communication

# Ferromagnetism and Chirality in Two-Dimensional Cyanide-Bridged Bimetallic Compounds

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Received May 16, 2002

The combination of hexacyanoferrate(III) anions, $[Fe(CN)_6]^{3-}$, with nickel(II) complexes derived from the chiral ligand *trans*-cyclohexane-1,2-diamine (*trans*-chxn) affords the enantiopure layered compounds $[Ni(\textit{trans}\text{-}(1S,2S)\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (**1**) and $[Ni(\textit{trans}\text{-}(1R,2R)\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (**2**). These chiral systems behave as ferromagnets ($T_c = 13.8$ K) with a relatively high coercive field ($H_c = 0.17$ T) at 2 K. They also exhibit an unusual magnetic behavior at low temperatures that has been attributed to the dynamics of the magnetic domains in the ordered phase.

The development of synthetic procedures for the assembly of spin carriers in an infinite lattice with high structural dimensionality and connectivity has been exploited during the past decade in the design of molecule-based magnets.[2] A remarkable example in this context is given by a family of compounds derived from the reaction between hexacyanometalate anions, $[M(CN)_6]^{n-}$, and different polyamine nickel(II) complexes.[3] An added value of this molecular approach is that it makes possible the synthesis of materials that combine magnetism with a second physical property that can be also cooperative, like electrical conductivity,[4] or second-order optical nonlinearity.[5]

An important property of molecules in this respect is chirality. In fact, optical activity can arise in a natural way (from chiral compounds) or can be magnetically induced (Faraday effect). The link between these two phenomena was discovered recently by Rikken and Raupach, who observed a small magnetochiral dichroism (MChD) in a chiral paramagnetic material.[6] Larger effects are expected for materials combining chirality and magnetic order. To date, there is no evidence for the observation of large MChD, even if a few chiral magnetic materials have already been reported.[7]

With these ideas in mind, we focused our attention on nickel(II) complexes based on chiral diamines and their reaction with hexacyanometalate anions. To date, there is only one example of a chiral ferromagnet based on this approach.[8] We have recently reported the reaction of the complex $[Ni(\textit{trans}\text{-}(1R,2R)\text{-chxn})(\textit{trans}\text{-}(1S,2S)\text{-chxn})(H_2O)_2]$[9] (*trans*-chxn = *trans*-cyclohexane-1,2-diamine) with $K_3[Fe(CN)_6]$ to yield the layered ferromagnet $[Ni(\textit{trans}\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (containing equal amounts of the two enantiomers randomly distributed over the whole lattice).[10] This prompted us to study the synthesis of the chiral analogues $[Ni(\textit{trans}\text{-}(1S,2S)\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (**1**) and $[Ni(\textit{trans}\text{-}(1R,2R)\text{-chxn})_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (**2**) by combination of the enantiomerically pure tris-diamine nickel(II) perchlorates with stoichiometric amounts of $[Ni(H_2O)_6](ClO_4)_2$ and $K_3[Fe(CN)_6]$.[11]

Compounds **1** and **2** are isostructural and crystallize in the non-centrosymmetric *P*1 space group.[12] Both compounds

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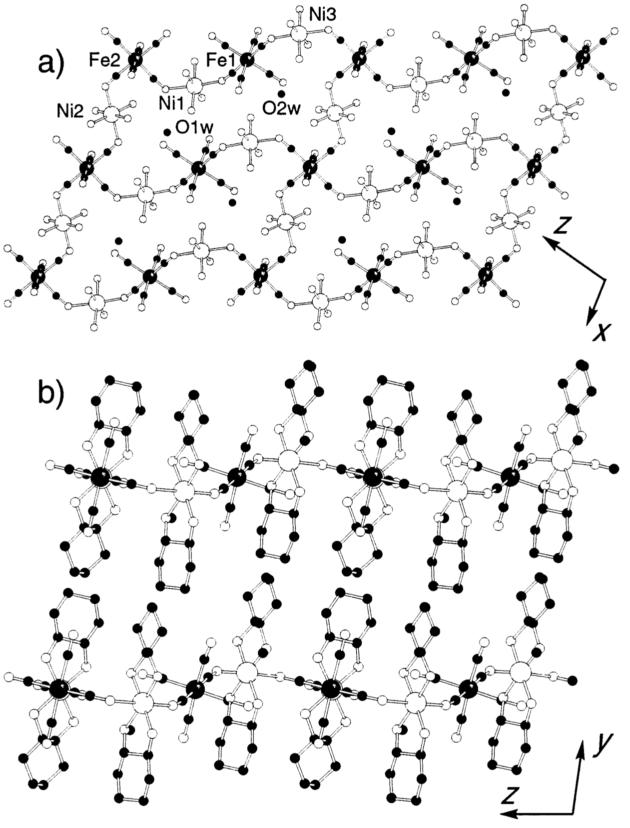

**Figure 1.** (a) Projection of the crystal structure of **1** onto the *ac* plane (cyclohexane rings have been omitted for clarity) showing the numbering scheme for significant atoms. (b) View along the *a* axis showing the arrangement of the layers in the *y* direction. Selected bond distances and angles: Ni1−NC(Fe1), 2.090(9) Å; Ni1−NC(Fe2), 2.166(9) Å; Ni2−NC(Fe2), 2.145(9) Å; Ni2−NC(Fe2), 2.138(9) Å; Ni3−NC(Fe1), 2.105(8) Å; Ni3−NC(Fe2), 2.194(9) Å; Ni1−N−C(Fe1), 150.3(8)°; Ni1−N−C(Fe2), 128.6(9)°; Ni2−N−C(Fe2), 121.2(8)°; Ni2−N−C(Fe2), 125.0(8)°; Ni3−N−C(Fe1), 146.6(8)°; Ni3−N−C(Fe2), 128.0(9)°.

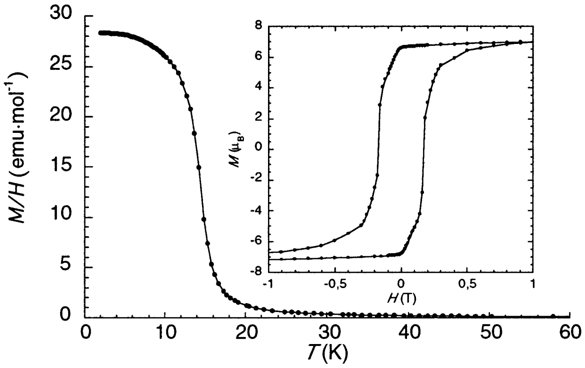

**Figure 2.** Thermal variation of the *M*/*H* ratio of **1** in a field of 1000 G. Inset: Hysteresis plot measured at $T = 2$ K.

have a two-dimensional (2D) structure with (12, 4) topology. A projection of the crystal structure of **1** (Figure 1a) onto the *ac* plane shows a planar rhomboidal grid of iron atoms (Fe2) belonging to $[Fe(CN)_6]^{3-}$ anions that bind to four adjacent *trans*-[Ni(*trans*-(1*S*,2*S*)-chxn)$_2$] moieties in a $\eta^4$-mode. One of these nickel ions (Ni2) is located roughly at the center of the short sides of the grid. The long sides of the grid are occupied by a Ni1−NC−Fe1−CN−Ni3 trimer, with a central iron atom sitting exactly along the grid and corresponding to a $\eta^2$-$[Fe(CN)_6]^{3-}$ unit that is hydrogen-bonded to two water molecules. It is worth mentioning the extremely bent Ni−N−C angles (with values ranging between 150.3° and 121.2°) as compared to similar compounds.[3,13] The overall structure can be described as layers of dodecanuclear cyclic units in which alternating *trans*-[Ni(*trans*-(1*S*,2*S*)-chxn)$_2$] cations and $[Fe(CN)_6]^{3-}$ anions are linked by $CN^-$ bridges.[13] A view parallel to the layers (Figure 1b) shows that all iron atoms and Ni2 lie in the same *ac* plane, while Ni1 and Ni3 are located at 0.800(3) Å above and 0.921(2) Å below this plane, respectively. The bulky cyclohexane rings are also arranged at both sides of the layer, giving rise to a large interplane distance of 12.639 Å. Only one enantiomeric form is present in the structure, and all chelate rings adopt the same $\lambda$ conformation.

Magnetic susceptibility ($\chi_m$) measurements were performed between 2 and 300 K on polycrystalline samples of **1** and **2**. Both enantiomers exhibit identical magnetic behavior. At 300 K, the product of molar magnetic susceptibility with temperature ($\chi T$) of the *S,S* isomer **1** equals 4.69 emu·K·mol$^{-1}$, in good agreement with the expected value for isolated spins. In the 50−300 K range, the reciprocal susceptibility follows a Curie−Weiss law with $\theta = 24.4$ K, indicating the presence of ferromagnetic interactions between adjacent Fe(III) and Ni(II) ions. Below 15 K, the magnetization (*M*) increases abruptly (Figure 2) and saturates to a value $M/H = 28.3$ emu·mol$^{-1}$. This behavior points to the existence of a long-range ferromagnetic ordering. Specific heat measurements unambiguously confirmed the magnetic ordering by the presence of a $\lambda$ peak at $T_c = 13.8$ K. The ordered phase was characterized by ac susceptibility measurements between 2 and 20 K (Figure 3). The in-phase component increases sharply below 15 K and exhibits a frequency-independent maximum around $T_c$. Below $T_c$, an out-of-phase signal appears. This signal shows a frequency-dependent broad

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(11) Single crystals of compounds **1** and **2** were grown by slow diffusion of the precursors in a water/acetonitrile mixture. Anal. Calcd for $C_{48}H_{88}Fe_2N_{24}Ni_3O_2$ (**1**): C, 43.64; H, 6.71; N, 25.44. Found: C, 43.56; H, 6.49; N, 25.26. IR (KBr, cm$^{-1}$): $\nu = 3339, 3277$ (N−H); 2919, 2847 (C−H); 2105 (C≡N). Anal. Calcd for $C_{48}H_{88}Fe_2N_{24}Ni_3O_2$ (**2**): C, 43.64; H, 6.71; N, 25.44. Found: C, 43.46; H, 6.63; N, 25.34. IR (KBr, cm$^{-1}$): $\nu = 3334, 3283$ (N−H); 2924, 2858 (C−H); 2105 (C≡N).

(12) Crystallographic data for **1**: $C_{48}H_{88}Fe_2Ni_3N_{24}O_2$, $M = 1321.25$, $P1$, $a = 9.0917(8)$ Å, $b = 12.6682(12)$ Å, $c = 14.9606(14)$ Å, $\alpha = 99.107(11)°$, $\beta = 93.897(11)°$, $\gamma = 109.239(11)°$, $V = 1593.0(3)$ Å$^3$, $Z = 1$, $\rho_{calcd} = 1.377$ Mg m$^{-3}$. $\lambda$(Mo K$\alpha$) = 0.71073 Å, $T = 153(2)$ K. R1 ($I > 2\sigma(I)$) = 0.0329, wR2 = 0.0583 (all data) with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)2/\sum w(F_o^2)^2)^{0.5}$. The absolute structure parameter was −0.02(2). Crystallographic data for **2**: $C_{48}H_{88}Fe_2Ni_3N_{24}O_2$, $M = 1321.25$, $P1$, $a = 9.0858(10)$ Å, $b = 12.6638(15)$ Å, $c = 14.9822(16)$ Å, $\alpha = 98.900(10)°$, $\beta = 93.950(10)°$, $\gamma = 109.45(10)°$, $V = 1592.4(3)$ Å$^3$, $Z = 1$, $\rho_{calcd} = 1.378$ Mg m$^{-3}$. $\lambda$(Mo K$\alpha$) = 0.71073 Å, $T = 153(2)$ K, $\mu = 1.371$ mm$^{-1}$, R1 ($I > 2\sigma(I)$) = 0.0604, wR2 = 0.1507 (all data) with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)2/\sum w(F_o^2)^2)^{0.5}$. The absolute crystal structure was determined by the Flack method (Flack number = 0.00(4)).

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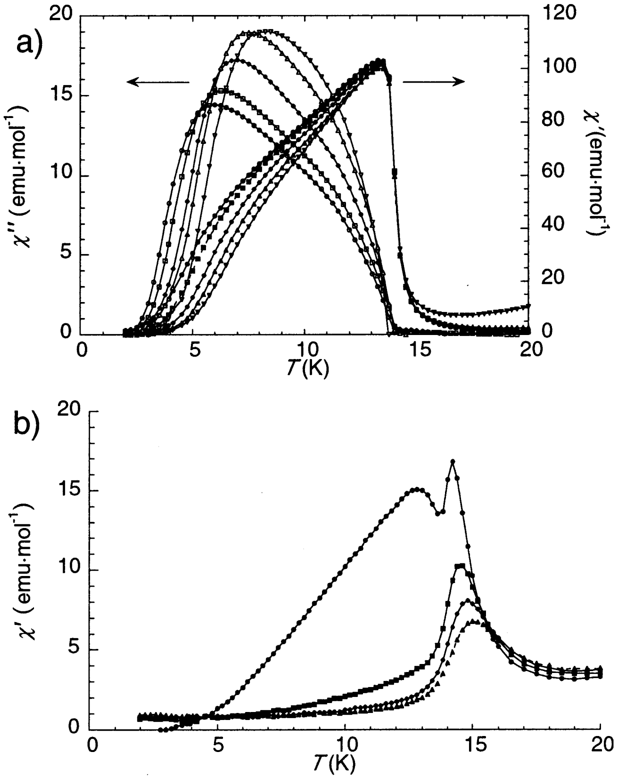

**Figure 3.** (a) Thermal variation of the ac susceptibility of **1** ($\chi'$, filled symbols; $\chi''$, empty symbols) at frequencies of 1, 10, 110, 332, and 997 Hz (circles, squares, rhombuses triangles (up), and triangles (down), respectively). (b) Thermal variation of $\chi'$ (332 Hz) for **1** at fields of 250, 500, 750, and 1000 G (circles, squares, rhombuses, triangles (up), and triangles (down), respectively).

maximum in the 5−10 K range that has to be attributed to the dynamics of the magnetic domains in the ordered phase. The frequency dependence of this maximum follows an Arrhenius law with an activation energy of 156 K. This peculiar behavior has been observed in both isomers **1** and **2** and indicates that the movement of the domain walls is strongly hindered in the ferromagnetic phase. In fact, the broad feature in the ac susceptibility curve vanishes under the presence of an applied continuous low field (Figure 3b). The hysteresis curve performed at 2 K is typical of hard magnets and shows the presence of steps at low field values. The first magnetization curve (Figure 2 inset) shows rapid saturation to reach a value of 7.7 $\mu_B$ at 5 T. This value is very close to the one expected ($\geq 8\ \mu_B$) for a ferromagnetic alignment of the interacting spins ($S_{Ni} = 1$, $S_{Fe} = {}^1/_2$; $S = 4$ per $Ni_3Fe_2$ formula).

An interesting point deserves special attention from the magnetic point of view. While most of these bimetallic systems are metamagnetic, compounds **1** and **2** are hard ferromagnets. The main factor that determines the ferro- or metamagnetic nature of the ordered phase is the interlayer separation. A well-known fact in 2D systems is that large interlayer distances favor a ferromagnetic ordering driven by dipolar interactions.[14] Probably, the presence of the bulky cyclohexyl groups separating the layers at large distances is responsible for the ferromagnetic character of the compounds.

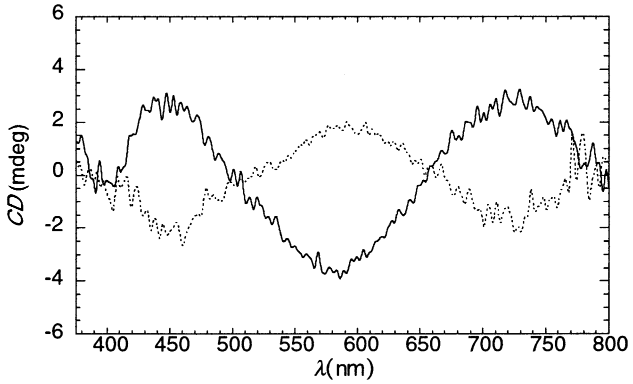

**Figure 4.** Circular dichroism spectra of **1** ($S$,$S$ isomer, continuous line) and **2** ($R$,$R$ isomer, dashed line) in KBr pellets.

Circular dichroism measurements (Figure 4) were used to confirm the enantiomeric nature of these optically active compounds. Compound **1** ($S$,$S$ isomer) exhibits positive Cotton effects at $\lambda_{max} = 450$ nm and $\lambda_{max} = 725$ nm and a negative dichroic signal centered at $\lambda = 585$ nm, while compound **2** ($R$,$R$ isomer) shows Cotton effects of the opposite sign at the same wavelengths. The signals observed in the visible region of the CD spectra can easily be assigned to d−d transitions, while the corresponding absorption spectra are dominated by a charge-transfer band located around 400 nm.

In summary, the present report illustrates the power of molecular chemistry in the design of systems combining different properties that can be easily modulated. The use of the chiral ligand *trans*-chxn in the synthesis of 2D bimetallic cyanide-bridged magnetic networks introduces optical activity as a new physical property in the magnetic system. It also modulates their magnetic behavior by increasing the interlayer distance and stabilizing the ferromagnetic phase. This is also at the heart of the dynamic behavior observed in the ferromagnetic phase, connected with the movement of the domain walls that are anchored at low temperatures. A thorough investigation of this chiral magnet, including neutron diffraction and MChD measurements, is in progress.

**Acknowledgment.** We thank Prof. Pérez-Payá for providing access to CD facilities. This work was supported by the European Union (TMR ERB 4061 PL97-0197) and the Ministerio de Ciencia y Tecnología (MCT) (Project MAT-2001-3507-C02-01). A.N. wishes to thank the Generalitat Valenciana for a Ph.D. fellowship. F.M.R. acknowledges a research contract from MCT (Programa “Ramón y Cajal”).

**Supporting Information Available:** Crystallographic data for compounds **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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