Unusual Magnetic Behavior in the Layered Ferromagnet $[Ni(C_6H_{14}N_2)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$

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The cyano-bridged molecular complex $[Ni(C_6H_{14}N_2)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$, with a rectangular 2D structure, displays long-range ferromagnetic ordering at 14 K, and exhibits unusual magnetic properties for this type of material, as confirmed by the appearance of two different peaks in the AC magnetic susceptibility plot, and a high coercive field (2.3 kOe) and remnant magnetization (6.8 μ_B).

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Cyanide-bridged bimetallic assemblies based upon hexacyanometalate building blocks, $[M(CN)_6]^{n-}$, constitute an extensive family of molecular-based materials with interesting magnetic and magneto-optical properties.[1−9] Bimetallic Prussian blue solids behave as magnets with high critical temperatures;[1] however, the face-centered cubic structures adopted by these phases result in a low magnetic anisotropy, and, furthermore, it is very difficult to obtain single crystals. One approach to overcome these problems is to synthesize materials based on $[M(CN)_6]^{n-}$ building blocks condensed with coordinatively unsaturated transition metal complexes such as $[Ni(L)_2]^{2+}$ (L = ethylenediamine derivative) or $[NiL]^{2+}$ (L = polyaza macrocyclic ligand). The resulting Ni_3M_2 (M^{III} = Fe, Cr) based polymeric complexes exhibit a remarkably diverse structural chemistry and a variety of cooperative properties including ferro-, ferri-, and metamagnetism. In fact, a slight modification of the ligand is sufficient to alter the structure, and hence the magnetic properties, completely. For instance, when ethylenediamine is used, a 1D rope-ladder structure is obtained, while the use of *N*-methylethylenediamine affords a 2D honeycomb sheet structure.[10] Interestingly, in the layered materials, a tuning of the bulk magnetic properties can be achieved by changing the interlayer spacing: the behavior can be tuned from metamagnetic for a small spacing (less than 10 Å), to ferromagnetic for a larger spacing, due to the competition between intralayer ferromagnetic interactions with the interlayer antiferromagnetic dipolar interactions. This versatility encouraged us to explore the structure-directing role of diamine ligands exhibiting a larger spatial extension, for example 1,2-diaminocyclohexane, which should favor a larger interlayer spacing and thus a ferromagnetic ordering.

Slow interdiffusion of $K_3[Fe(CN)_6]$ and $[Ni(L)_2]Cl_2$ (L = *trans*-1,2-diaminocyclohexane) in water afforded large brown crystals of $[Ni(C_6H_{14}N_2)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$.[11] The structure consists of a neutral network of bimetallic cyanide layers that are decorated with organic cyclohexane groups projecting above and below into the interlamellar region.[12] This double layer of bulky diamine ligands imposes a large intersheet separation, with Ni−Ni or Fe−Fe interlayer distances equal to 12.639 Å and a shorter Ni−Fe interlayer distance of 10.889 Å (Figure 1, top). The layers are composed of deformed rectangular grids of twelve octahedral metal sites in which alternating *trans*-$[Ni(C_6H_{14}N_2)_2]^{2+}$ cations and $[Fe(CN)_6]^{3-}$ anions are linked by CN^- bridges (Figure 1, center). Water molecules occupy the free space within these rectangular grids. In contrast with the other 12-gon motifs reported recently,[13] in the present case there are two distinct $[Fe(CN)_6]^{3-}$ units, situated at the corners and at the center of the sides of the grid, which act as tetradentate and bidentate ligands connecting four and two *trans*-$[Ni(C_6H_{14}N_2)_2]^{2+}$ complexes, respectively. Another unusual feature is the extremely bent Ni−N−C bond angles. In related compounds reported so far, the lowest values have been found to be around 148°.[14] Only copper-containing compounds have shown a lower angle for bridging cyanides, near 120°.[15] However, values as low as 128.69° and 122.53° for Ni1−N2−C2 and Ni2−N3−C3, respectively, are observed in the title compound (Figure 1, bottom).

The magnetic susceptibility of the bimetallic compound, measured on polycrystalline samples in the temperature

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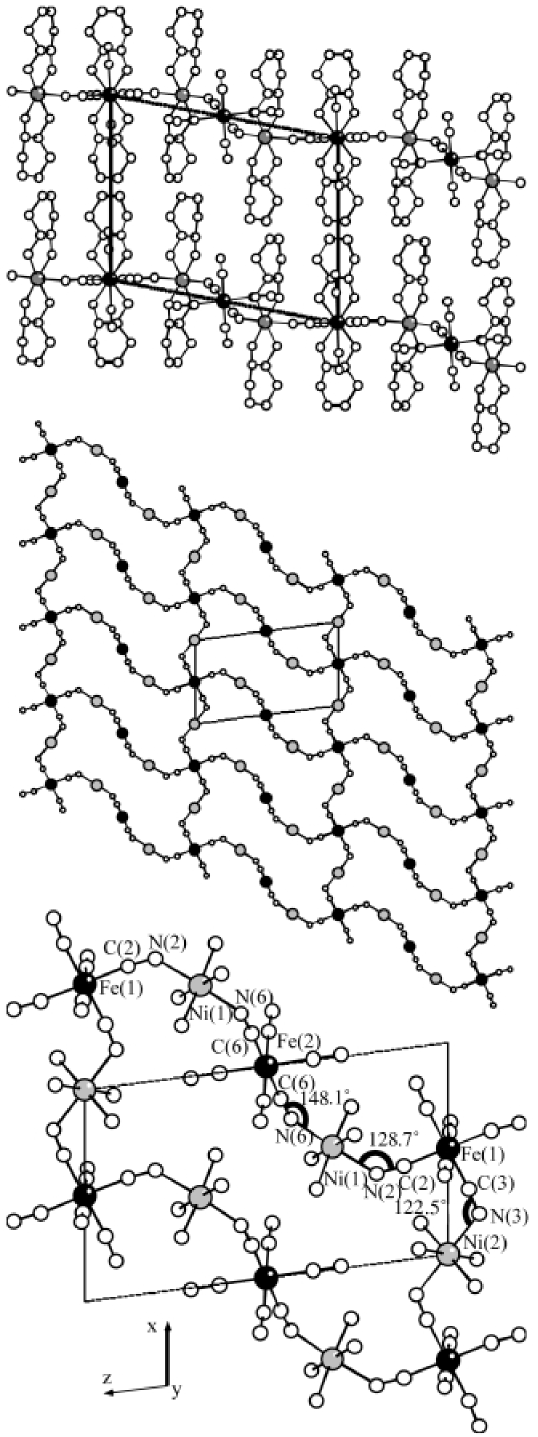

Figure 1. Top: View of the structure of the title compound showing the layers in the *ac* plane. Center: Schematic view of the layers in the *ab* plane. Bottom: View of the Fe_6Ni_6 ring showing the distortions in the bridging Ni−N−C bridges; the cyclohexane rings have been omitted for the sake of clarity (Fe atoms in black and Ni atoms in gray); selected distances in Å: Fe(1)−C(2) 2.088(3), Fe(1)−C(3) 1.916(4), Ni(1)−N(2) 2.168(3), Ni(1)−N(6) 2.088(3), Ni(2)−N(3) 2.154(3), Fe(2)−C(6) 1.931(4)

range 2−300 K under a field of 1000 Oe, follows a Curie−Weiss law above 50 K with a Weiss constant θ of 21.1 K. The positive sign of θ indicates the presence of dominant ferromagnetic interactions between neighboring Fe^{III} and Ni^{II} ions. Below 15 K, χ_m increases sharply and saturates at a lower temperature. In addition, the zero field cooled (ZFC) and field cooled (FC) measurements of the DC magnetic susceptibility deviate from each other at 14 K (Figure 2, inset), with the remnant magnetization disappearing below this temperature. This behavior suggests the onset of a long-range ferromagnetic transition.

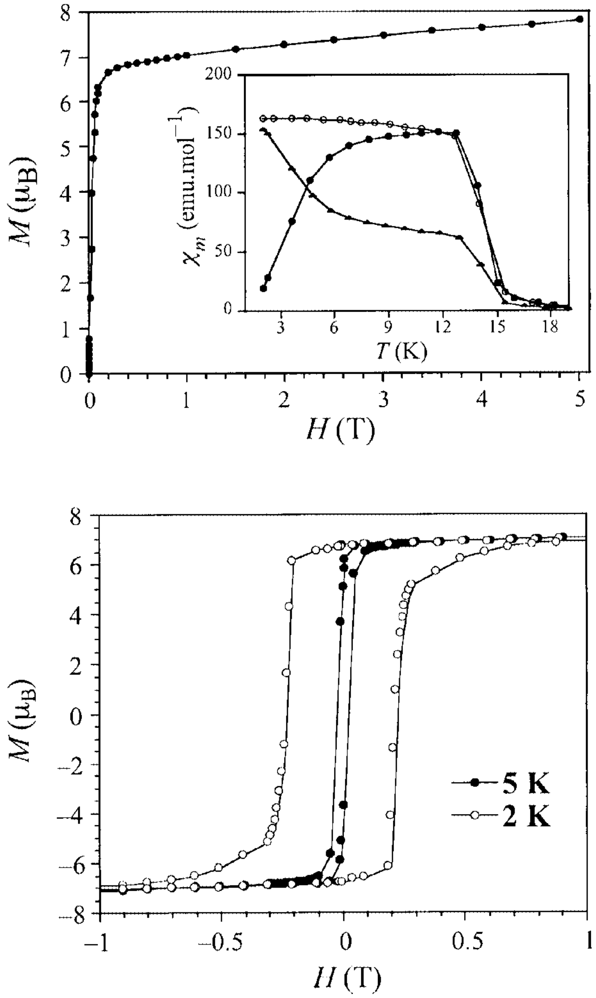

Figure 2. Top: Field dependence of the magnetization at 2 K for the title compound; inset: zero-field cooled (full circles) and field cooled (empty circles) plots of the DC magnetic susceptibility at 1 G, and remnant magnetization (triangles). Bottom: Hysteresis loop for the title compound at 2 and 5 K

The nature of the magnetic transition was confirmed by the field dependence of the isothermal magnetization performed at 2 K (Figure 2). In fact, a rapid increase of the magnetization to a value of ca. 6.5 μ_B is observed at 1 kOe, and increases to 7.7 μ_B at 50 kOe. This latter value is slightly smaller than, but very close to, 8 μ_B, which is the expected value for a ferromagnetic alignment of the interacting spins in the Ni_3Fe_2 unit ($S_{Ni} = 1$, $S_{Fe} = 1/2$; $S = 4$ per Ni_3Fe_2 unit). Hence, the compound behaves as a ferromagnet, although the lower than expected saturation value suggests the presence of some spin canting.

At 2 K this ferromagnet exhibits magnetic hysteresis with a coercive field as large as 2.3 kOe and a high remnant magnetization of 6.8 μ_B per Ni_3Fe_2 unit. This leads to an energy product of 7.3 $kJ{\cdot}m^{-3}$, which is similar to that obtained in very hard magnetic materials. To the best of our knowledge, the only precedent for a structurally characterized Ni_3Fe_2 ferromagnet is the recently reported layered compound $[NiL]_3[Fe(CN)_6]_2{\cdot}12H_2O$ (L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane),[13a] which orders ferromagnetically at 9.1 K. At T = 1.6 K, the material exhibits a coercive field of 1.5 kOe and a remnant magnetization of 1.36 μ_B. In our new layered magnet, the coercivity is larger and the energy product is about one order of magnitude bigger.

One main feature of note in this study is the observation that the Ni^{II} and Fe^{III} centers are ferromagnetically coupled, in spite of the fact that the Ni−N−C angles are much more acute than those reported for known cyanide compounds of these two metals.[14] Our findings underscore the fact that there is a wide range of angles that stabilize a ferromagnetic $Ni^{II}-Fe^{III}$ coupling through a CN^- bridge.

In order to determine precisely the critical temperature at which this transition occurs AC magnetic measurements were performed (Figure 3). We observed a sharp increase below ca. 15 K and a broad and asymmetric maximum in the real part of the susceptibility, χ_m', at about 13.5 K. This signal is accompanied by an out-of-phase signal, χ_m'', that becomes non-zero below a temperature of 14.0 K, which defines T_c. Interestingly, the χ_m'' signal displays a shoulder at ca. 12 K, which is frequency independent, and a maximum at ca. 4 K which is strongly frequency dependent (Figure 3). This result, together with the observation that the compound behaves as a hard magnet only below 5 K (at higher T the coercive field is very small), indicates that the movement of the domain walls is strongly hindered below this temperature. The very same features were observed when measurements were performed on a single crystal. This proves that the anomalous behavior is actually intrinsic for this compound, and not sample dependent.

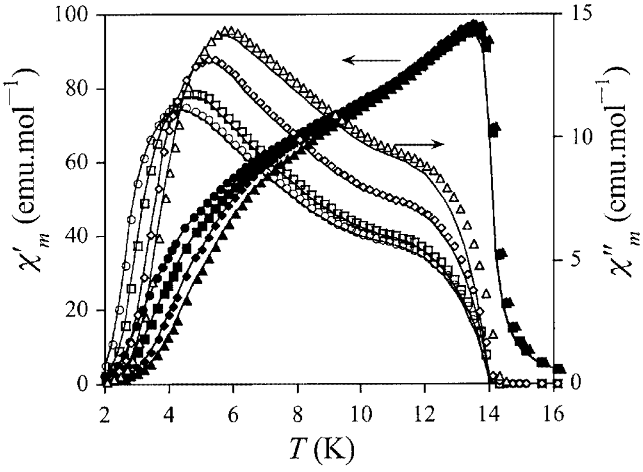

Figure 3. Thermal variation of the molar AC magnetic susceptibility for the title compound (χ': filled symbols, χ'': empty symbols) at frequencies of 1, 10, 110 and 332 Hz (circles, squares, diamonds and triangles, respectively) showing the frequency dependence of χ'' in the peak around 4 K and the appearance of a χ'' signal below 14.0 K

A plausible explanation of this behavior would be that the magnetic transition at 14.0 K corresponds to a ferromagnetic ordering within the magnetic layer that it is triggered by the magnetic anisotropy of the metallic ions. At lower temperatures (below 5 K), the dipolar coupling between layers becomes relevant and induces an anchoring of the domain walls. If this is the case, the frequency dependence of χ'' can be related to the activation energy required to unblock these domain walls.[16] Fortunately, since this compound can be grown as well-shaped single crystals, a more detailed physical characterization, including neutron diffraction, can be performed that will provide detailed information on the anisotropy and magnetic phase diagram of this novel molecule-based ferromagnet. The unusual features observed in the AC magnetic susceptibility measurements are similar to those observed in other layered magnets with large interlayer separations,[17] suggesting that these effects should be related to the low dimensionality of these systems. Molecular layered magnets are ideal to study this novel behavior since the interlayer separation of a given system can easily be tuned simply by changing the spacers in each case.

Finally, it is worth mentioning that a racemic mixture of the ligand *trans*-1,2-diaminocyclohexane was used for the synthesis of the title compound and therefore both stereoisomers are present, yielding a centrosymmetric solid state structure. The organic ligands are disordered in two different crystallographic positions corresponding to the two stereoisomers, due to statistical distribution. More work is in progress to obtain a pure enantiomeric structure that would be of interest to study possible magneto-chiral effects.[10] In this case the chirality appears only in the organic ligand and not in the metallic complexes, therefore more subtle effects could be expected.

Experimental Section

Synthesis: The precursor $[Ni(C_6H_{14}N_2)_2]Cl_2$ was prepared by the literature method developed for ethylenediamine complexes.[19] All reagents were of commercial grade and used without further purification.

$[Ni(C_6H_{14}N_2)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$ (1): A solution containing 1,2-diaminocyclohexane (2 mmol, 245 mL) in 40 mL of methanol was added to an aqueous solution of $NiCl_2{\cdot}6H_2O$ (2 mmol, 476 mg) in 60 mL of water. A solution of $K_3[Fe(CN)_6]$ (1.3 mmol, 439 mg) in 60 mL of water was then added dropwise to the resulting brown solution,. A brown precipitate was filtered off and the yellow filtrate was allowed to stand in the dark overnight. Brown plates were collected by suction filtration and washed with water and ethanol. Single crystals suitable for X-ray single crystal analysis were obtained after a week by slow diffusion of $[Ni(C_6H_{14}N_2)_2]Cl_2$ (102 mg, 0.28 mmol) and $K_3[Fe(CN)_6]$ (94 mg, 0.28 mmol) placed in the sides of an H-type diffusion tube. Water (55 mL) was used as solvent.

Physical Measurements: X-ray data sets were collected on a SMART 1K area detector diffractometer equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The frames were integrated in the Siemens SAINT[20] software package and the data were corrected for absorption using the SADABS program.[21] The structure was solved by direct methods followed by Fourier synthesis (SIR-97),[22] and refined on F^2 (SHELXL-97).[23] Variable temperature susceptibility measurements were carried out in the temperature range 2−300 K at a magnetic field of 0.1 T on polycrystalline samples with a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. Susceptibility data were corrected from the diamagnetic contributions of the compound as deduced from Pascal's constant tables. Isothermal magnetization measurements at low temperatures were carried out up to 5 T on the same apparatus.

Acknowledgments

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