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Metamagnetism of the First Cyano-Bridged Two-Dimensional Brick-Wall-like 4f−3d Array

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There has been continuing interest in the magnetochemistry of the cyano-bridged Prussian Blue analogues.[1] Some exciting results have been reported, such as the finding that some transition metal cyanides exhibit long-range magnetic ordering above room temperature.[1c] It should be noted that, until now, great emphasis has been placed on magnetic studies of cyano-bridged transition metal assemblies. We have now turned our attention to synthesizing cyano-bridged lanthanide−transition metal complexes, and to investigating their magnetic properties. It is known that the f-block atoms exhibit large and anisotropic magnetic moments and can form hard magnets when incorporated into the solids. In 1976, a series of cyano-bridged three-dimensional rare-earth hexacyanometalates(III) $LnM(CN)_6{\cdot}nH_2O$ (M = Fe or Cr, n = 4 or 5) were crystallized and subjected to single-crystal X-ray and magnetic susceptibility measurements.[2] Ferrimagnetic ordering was observed for $LnCr^{III}(CN)_6{\cdot}nH_2O$ (Ln = Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm). Incorporation of organic ligands into the three-dimensional 4f−3d complexes can reduce the dimensionality of the parent complexes and give various molecular structures.[3−5] It has been found that the reactions of diamagnetic $K_2[M(CN)_4]$ (M = Ni, Pd, and Pt) anions with anhydrous $LnCl_3$ or $LnCl_2$ in DMF (*N*,*N*-dimethylformamide) produce unusual cyano-bridged one-dimensional 4f−3d arrays in which DMF molecules are included as a capping ligand.[6] Introduction of DMF into $LnFe^{III}(CN)_6{\cdot}nH_2O$ gives a series of cyano-bridged 4f−3d dimers $[Sm(DMF)_4(H_2O)_4Fe(CN)_6]{\cdot}$

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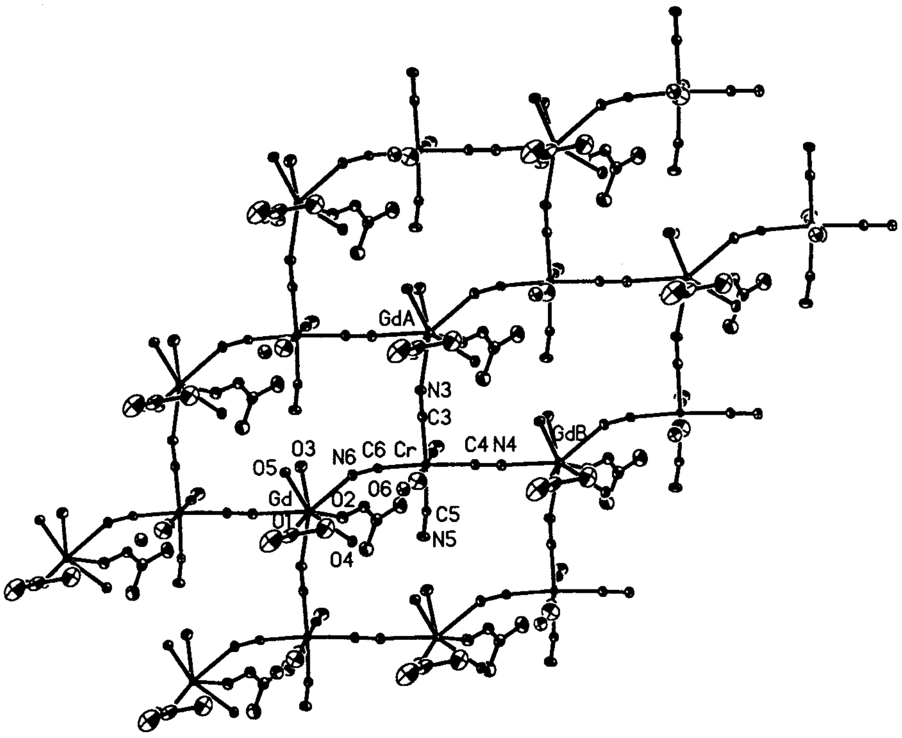

Figure 1. Structure of **1**. Selected bond distances (Å) and angles (°): Gd−O(2) 2.324(3), Gd−O(1) 2.340(3), Gd−O(5) 2.420(3), Gd−O(4) 2.426(3), Gd−O(3) 2.430(3), Gd−N(4)#1 2.491(4), Gd−N(6) 2.496(4), Gd−N(3)#2 2.496(4), C(6)−N(6)−Gd 154.1(4), C(4)#1−N(4)#1−Gd 174.9(4), C(3)#2−N(3)#2−Gd 167.5(4).

H_2O[4] or $[Ln(DMF)_4(H_2O)_3Fe(CN)_6]\cdot H_2O$ (Ln = lanthanide ions other than Sm and Nd).[5] Very recently, the pentanuclear cyano-bridged 4f−3d array $[Ho(H_2O)_3(DMF)_3]_2[Ni(CN)_4]_3$ was reported based on the reaction of $K_2[Ni(CN)_4]$ and $Ho(NO_3)_3\cdot 6.5H_2O$ in DMF.[7] To the best of our knowledge, no cyano-bridged two-dimensional 4f−3d assemblies with long-range magnetic ordering have been reported so far.[8] Hence, we sought to design, synthesize, and characterize the first such example. Considering that the aforementioned 4f−3d dimers were prepared in an excess of DMF, we employed a quantitative proportion of DMF (Ln:DMF = 1:2) in the hope of obtaining a two-dimensional array that might assume a grid-, honeycomb-, or brick-wall-like topology dependent on the mode of the M−C≡N−Ln linkages. We found that the reaction between $Gd(NO_3)_3\cdot H_2O$, DMF, and $K_3[Cr(CN)_6]$[9] in the molar ratio of 1:2:1 in H_2O affords the two-dimensional bimetallic complex $[Gd(DMF)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ (**1**),[10] which has a novel brick-wall-like structure.

X-ray crystallography[11] reveals that the structure consists of neutral layers with slightly distorted Cr_3Gd_3 rectangles. Each $[Cr(CN)_6]^{3-}$ unit uses three cyanide groups in the meridional arrangement to connect with three $[Gd(DMF)_2(H_2O)_3]^{2+}$ units (Figure 1). Each $[Gd(DMF)_2(H_2O)_3]^{2+}$ unit links three $[Cr(CN)_6]^{3-}$ ions, with the bridging cyanides and the bridged metal ions lying in a plane. This local molecular disposition extends to generate a flat brick-wall-like structure, which is the first cyano-bridged 4f−3d complex with such a topology. The bridging cyanide ligands coordinate to the gadolinium(III) ions in two different fashions: two nearly linear [Gd−N(4)#1−C(4)#1 = 174.9(4)°, Gd−N(3)#2−C(3)#2 = 167.5(4)°] and one bent [Gd−C6−N6 = 154.1(4)° (where #1 and #2 denote the symmetry transformations $x - 1, y - 1, z$ and $x, y - 1, z$, respectively)]. The Gd(III) ion exists in a slightly distorted square anti-prism coordination geometry with a dihedral angle between the two faces of 2.3(2)°. The adjacent Cr···Gd distances are 5.469(1) Å for Cr···Gd, 5.684(1) Å for Cr···Gd#3, and 5.692(1) Å for Cr···Gd#4, respectively (where #3 denotes the transformation $x, y + 1, z$ and #4 denotes $x + 1, y + 1, z$). The shortest interlayer metal−metal distance is 7.738(1) Å for Cr···Gd#5 (where #5 denotes $1 - x, 1 - y, -z$). The flat

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(10) To $Gd(NO_3)_3\cdot 6H_2O$ (0.5 mmol) in DMF (0.2 mL) was added $K_3[Cr(CN)_6]$ (0.5 mmol) in water (5 mL). The resultant yellow mixture was kept undisturbed in the dark at room temperature. After 1 week, large platelike yellow crystals were obtained. The complex is insoluble in inorganic and organic solvents except water. The IR spectrum of the complex shows two sharp bands (2157 and 2134 cm^{-1}) in the range 2000−2200 cm^{-1} that are attributed to C≡N stretching modes. The splitting of ν(C≡N) suggests the presence of both bridged and non-bridged CN$^-$ ligands. The strong band at 1663 cm^{-1} can be assigned to the C=O stretching vibration (DMF).

(11) Diffraction data were collected on a Nonius Kappa CCD diffractometer using Mo K$_\alpha$ radiation. All data were corrected for LP and empirical absorption effects. Crystal data for **1**: $[Gd(DMF)_2(H_2O)_3][Cr(CN)_6]\cdot H_2O$, $C_{12}H_{22}N_8O_6GdCr$, $M_w = 583.63$, $T = 293$ K, triclinic, space group P-1, $a = 7.7102(2)$, $b = 9.4112(2)$, $c = 16.2819(4)$ Å, $\alpha = 94.259(1)$, $\beta = 99.989(1)$, $\gamma = 100.990(2)$°, $U = 1135.14(5)$ Å^3, $Z = 2$, $\mu = 3.415$ mm^{-1}, R_1 [5046 observed reflections with $I > 2\sigma(I)$] = 0.0392, wR2 = 0.1040 (all data), GOF = 1.136 (277 parameters).

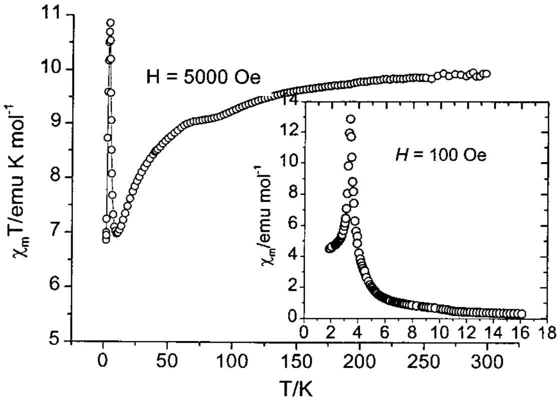

Figure 2. Temperature dependence of $\chi_M T$ for **1** measured at 5 kOe. Inset: Temperature dependence of χ_M in an applied field of 100 Oe for **1**.

layers align parallel, with separations of ca. 7.4(1) and 8.5(1) Å. The uncoordinated water molecules are positioned between the distantly separated layers and and linked to one terminal CN^- ligand of $[Cr(CN)_6]^{3-}$ and to the coordinated water molecules via hydrogen bonding. Between the closer layers, the nonbridging cyanide ligands interact with the coordinated water molecules through hydrogen bonds to connect the two layers.

The variable-temperature (2−300 K) magnetic susceptibilities of **1** have been measured on a crystalline sample in a field of 5 kOe. A plot of $\chi_m T$ vs T is shown in Figure 2, where χ_m is the magnetic susceptibility per GdCr unit. The $\chi_m T$ value at 300 K is ca. 9.4 emu K mol^{-1} (the spin-only value is 9.75 emu K mol^{-1}), which decreases smoothly with decreasing temperature, reaching a minimum value of 7.0 emu K mol^{-1} at 10.0 K. With a further decrease in temperature, $\chi_m T$ increases sharply, reaching a maximum value of 10.9 emu K mol^{-1} at 4.0 K before decreasing again. The magnetic susceptibility above 10.0 K obeys the Curie−Weiss law with a negative Weiss constant, θ, of −8.5 K, which suggests the occurrence of antiferromagnetic coupling between the adjacent Gd(III) and Cr(III) ions. The Curie constant, C, is equal to 10.2 emu K mol^{-1}, close to the expected value of 9.75 emu K mol^{-1} with $g = 2.0$. The magnetic susceptibilities of **1** measured in a 100-Oe field show an abrupt increase in χ_m at ca. 4.0 K (inset of Figure 2), suggesting a developed intralayer ferrimagnetic correlation as a result of the noncancellation of spins. The peak in the χ_m versus T curve at 3.5 K (inset of Figure 2) indicates a long-range antiferromagnetic (AF) ordering due to the AF interaction between the ferrimagnetic layers. The temperature dependence of the ac magnetic susceptibilities verifies the magnetic phase transition at ca. 3.5 K (T_N) and the absence of a frequency dependence.

The field dependence of the magnetization (0−30 kOe) measured at 1.8 K shows rapid saturation of the magnetization, reaching a saturation plateau of 4.0 Nβ per GdCr at 30 kOe, which is equal to the expected $S = 2$ value of 4 Nβ for a ferrimagnetic GdCr system. A hysteresis loop at 1.8 K (Figure 3) was observed with a very small coercive field of less than 10 Oe, typical of a soft magnet. The “double-S” shape of the curve is indicative of a metamagnet, which switches from an antiferromagnetic ground state to a ferrimagnetic-like state upon the application of a large enough field. The critical field is approximately 240 Oe at 1.8 K. This phenomenon is not uncommon for two-dimensional layered ferromagnetic bimetallic 3d complexes with interlayer antiferromagnetic interactions, but this is the first observation of it for two-dimensional cyano-bridged 4f−3d complexes.

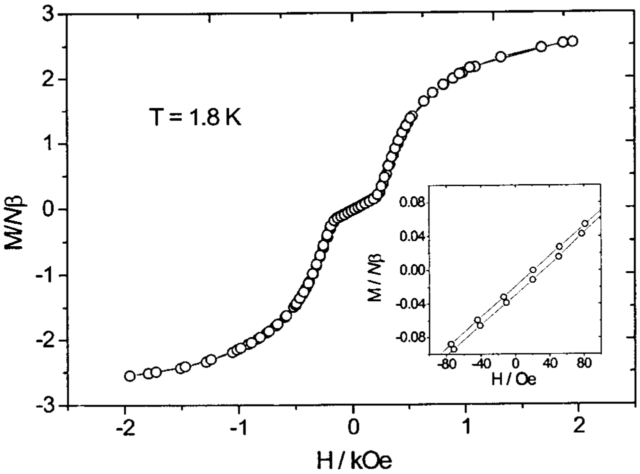

Figure 3. Hysteresis loop at 1.8 K for **1**. Inset: Expansion showing the very small coercivity.

In conclusion, we have successfully synthesized the first cyano-bridged two-dimensional brick-wall-like lanthanide−transition metal complex exhibiting long-range magnetic ordering at 3.5 K. The low coercive field might be enhanced by the alternation of lanthanide ions with a large magnetic anisotropy, Sm^{3+} for instance. Further work along this line is in progress in our laboratory.

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Supporting Information Available: Figures of the coordination polyhedron of the Gd(III) ion, projection along the *c* axis showing the brick-wall-like backbone, projection along the *b* axis showing the H-bonded 3D network, temperature dependence of χ_M^{-1} in an applied field of 5000 Oe, real (χ') and imaginary (χ'') ac magnetic susceptibilities in zero applied dc field and in an ac field of 2 Oe at different frequencies, field dependence (0−30 KOe) of magnetization at 1.8 K for **1** (PDF). Also see X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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