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Unexpected Assembly of a Unique Cyano-Bridged Three-Dimensional Cu_3Cr_2 Ferromagnet

Hui-Zhong Kou,[†] Song Gao,[*,†] Jing Zhang,[†] Ge-Hui Wen,[‡]
Gang Su,[§] R. K. Zheng,[‡] and X. X. Zhang[‡]

*State Key Laboratory of Rare Earth Materials
Chemistry and Applications
PKU-HKU Joint Laboratory on Rare Earth
Materials and Bioinorganic Chemistry
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871, China
Department of Physics
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong, China
Department of Physics
The Graduate School of the Chinese Academy of Sciences
P.O. Box 3908, Beijing 100039, China*

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Much attention is currently being devoted to the design and synthesis of molecular magnetic materials exhibiting spontaneous magnetization. The main synthetic strategy is virtually to use and connect two paramagnetic building blocks (bricks) to generate polynuclear or extended arrays. Extended arrays of high dimensionalities may exhibit higher ordering temperatures due to the increased number of interacting neighbors. A representative example is the cyano-bridged three-dimensional (3D) Prussian blue-type complexes constructed from hexacyanometalate(III) and simple transition metal building blocks.[1] One of these materials exhibits long-range magnetic ordering at T_c as high as 372 K.[1c] Thus far, a number of Prussian blue analogues of different dimensionalities have been synthesized and characterized structurally and magnetically.[2,3] These studies have shown that the low-dimensional materials have T_c values generally lower than that of the corresponding 3D analogues, and the few hybrid 3D arrays derived from paramagnetic $[M(CN)_6]^{3-}$ and transition metal complexes order at different temperatures depending on the average number of the nearest neighbors around a given metal ion.[2b,e,l] Since copper(II) ion exhibits great stereochemical plasticity, a large variety of magnetic compounds with hexacyanometalates may be fabricated using Cu(II). Nevertheless, only a few such bimetallic complexes have been reported so far, and most of them were synthesized by the reaction of hexacyanometalate with CuL^{2+} complexes containing only two available coordination sites, producing low-dimensional species.[3] It is worth mentioning that the only complex exhibiting the magnetic phase transition at 11.0 K is $[Cu(en)]_3[Fe(CN)_6]_2\cdot 3H_2O$, whose structure is suggested to be 3D.[3g] To gain an explicit structure−property correlation, we extended this study to a Cu_3Cr_2 analogue. Here we report a unique 3D coordination polymer $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$ **1** with ferromagnetic ordering below 57 K.

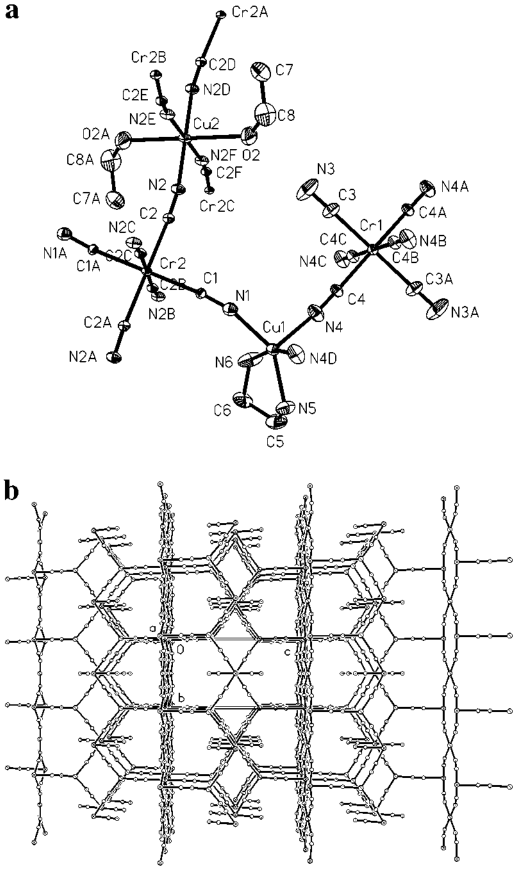

Figure 1. (a) The asymmetric unit of **1**. (b) Projection of **1** along the *a*-axis showing the tunneled molecular structure.

Small blue single crystals of **1** are formed reproducibly by slow diffusion of $Cu(en)(H_2O)_2SO_4$[4] in H_2O into $K_3[Cr(CN)_6]$[5] in a H_2O−EtOH (2:1) mixture after a few months. X-ray crystallography[6] reveals that **1** consists of a 3D polymer $\{[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2\}_\infty$, as shown in Figure 1. The asymmetric unit of the structure is composed of two independent $[Cr(CN)_6]^{3-}$ units (Cr(1) and Cr(2)), and two different types of Cu(II) centers in $[Cu(en)]^{2+}$ (Cu(1)) and $[Cu(EtOH)_2]^{2+}$ (Cu(2)), respectively. Each Cr(1) ion connects to four $[Cu(en)]^{2+}$ moieties (Cu(1))

[†] Peking University.

[‡] The Hong Kong University of Science and Technology.

[§] The Graduate School of the Chinese Academy of Sciences.

(1) For example: (a) Verdaguer, M. *Science* **1996**, *272*, 698. (b) Sato, O.; Iyoda, T.; Fujishima. A.; Hashimoto, K. *Science* **1996**, *272*, 704. (c) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593. (d) Hatlevik, Ø.; Buschmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914.

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(6) Crystal data for **1**: $[Cu(EtOH)_2][Cu(en)]_2[Cr(CN)_6]_2$, $C_{20}H_{28}N_{16}O_2Cu_3Cr_2$: M_w = 819.20, T = 293 K, monoclinic, space group $P2/m$, a = 7.1843(3), b = 7.5210(3), c = 14.4763(5) Å, β = 94.401(3)°, U = 779.89(5) Å^3, Z = 1, μ = 2.734 mm^{-1}, R_1 [1798 observed reflections with $I > 2\sigma(I)$] = 0.0465, wR_2 = 0.1133 (all data), GOF = 1.060 (134 parameters).

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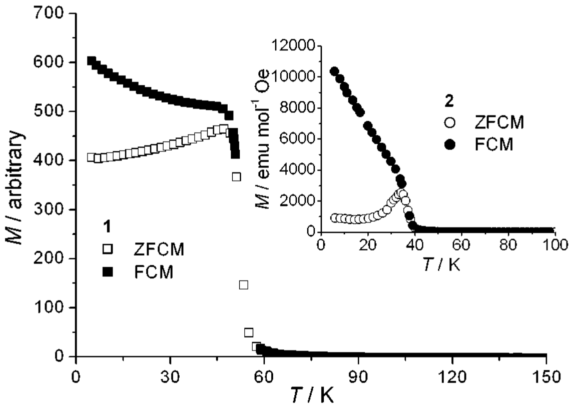

Figure 2. Plots of field-cooled magnetization (FCM), zero-field-cooled magnetization (ZFCM) vs temperature measured at 20 Oe for **1** and **2** (Inset).

through order CN^- bridges with two CN^- ligands intact. Each Cr(2) center uses four cyano ligands within the *ab* plane to bridge four *trans*-$[Cu(EtOH)_2]^{2+}$ (Cu(2)) units, while the remaining two *trans*-cyano ligands coordinate to two $[Cu(en)]^{2+}$ (Cu(1)) groups along the *c* direction. The Cu(1) atom is five-coordinate, with three cyano nitrogen atoms of three different $[Cr(CN)_6]^{3-}$ units and two other nitrogen atoms of en. The Cu(2) atom exhibits an elongated octahedral environment with four cyano nitrogen atoms in the equatorial plane and two oxygen atoms at axial positions [Cu(2)−O(2) = 2.390(5) Å]. The resulting 3D network can be described as grid-like $\{[Cu(EtOH)_2]_2Cr(CN)_6\}_\infty$ layers (*ab* plane) which are connected by $\{[Cu(en)]_2Cr(CN)_6\}_\infty$ chains (along *b* direction). The arrangement of the grid layers and chains yields a tunneled 3D motif. The adjacent Cr···Cu distances are 5.237 Å for Cr(1)···Cu(1), 5.129 Å for Cr(2)···Cu(1) and 5.200 Å for Cr(2)···Cu(2), respectively.

Since the yield of **1** is very low, another complex of formula $[Cu(H_2O)_2][Cu(en)]_2[Cr(CN)_6]_2 \cdot H_2O$ **2** was synthesized. Powder XRD analysis and magnetic properties (vide infra) show that **2** has a structure different from **1**, although they could have similar linking mode of CN^- based on their IR spectra ($\nu_{C\equiv N}$: 2173, 2108 cm^{-1} for **1**; 2169, 2107 cm^{-1} for **2**). Magnetic studies of **1** (on a few single crystals less than 0.4 mg) and **2** were performed on an MPMS SQUID and a MagLab 2000 magnetometer. The increase of $\chi_m T$ with decreasing temperature above 70 K confirms the ferromagnetic interactions between adjacent Cu(II)···Cr(III) ions. The zero-field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) curves of **1** measured in a low field of 20 Oe show an abrupt increase in *M* at ca. 57 K, indicating the occurrence of spontaneous magnetization as shown in Figure 2, while **2** exhibits ferromagnetic ordering at ca. 40 K (Inset of Figure 2), in good agreement with the results of the *ac* magnetic susceptibilities.

The field dependence of the magnetization (0−50 kOe) of **2** measured at 2.0 K shows a rapid saturation of the magnetization at ca. 10 kOe, and reaching 9.05 $N\beta$ per Cu_3Cr_2 at 50 kOe which is very close to the value of 9 $N\beta$ for a ferromagnetic Cu_3Cr_2 system with $S_T = {}^9/_2$. Hysteresis is observed with coercive fields (H_c) of 230 Oe at 1.8 K, 200 Oe at 3.0 K and 180 Oe at 10 K, respectively. However, no hysteretic behavior is observed in **1**. The distinct H_c for **2** may be due to its very fine particle size of the sample, as evidenced by the wide XRD peaks. Better crystallization of **1** compared with **2** might favor a higher T_c.[1c]

To estimate the magnetic exchange integral (*J*) between Cu(II) and Cr(III) in **1**, we used the expression derived by Verdaguer et al. based on Neel's molecular field theory as given below,[7]

$$kT_c = (Z|J|/N\beta^2 g^2)\sqrt{C_{Cu}C_{Cr}}$$

where *k* is Boltzmann's constant, *Z* the number of magnetic neighbors, *N* the Avogadro constant, *g* the mean Landé factor, β the Bohr magneton, C_{Cu} and C_{Cr} the Curie constants of Cu(II) and Cr(III) ($C_i = S_i(S_i + 1)$, if S_i is the spin on site *i*). The average *Z* value for **1** is 4, T_c is 57 K, and then the *J* value is estimated to be 6 cm^{-1}. Although it appears to be smaller than the value of 9.16 cm^{-1} for the tetranuclear complex $[Cu(edma)]_3Cr(CN)_6$,[3e] the assembly of the two kinds of metal ions in the 3D solid makes it a long-range ordering magnet with considerably high T_c.

The present research illustrates the structural diversity of magnetic materials containing hexacyanometalate(III) and copper(II) building blocks. The peculiar coordination mode of the Cu(II) ion contributes to the formation of the unexpected interesting structure. Additionally, the loss of en ligand from $[Cu(en)]^{2+}$ is entirely unexpected, since the chelating en ligand should form stable Cu(II) complexes. A long-range ferromagnetic ordering below 57 K is observed as expected for a 3D system. It is noteworthy that the present complex is the first structurally characterized Cu(II)-containing Prussian blue analogue with spontaneous magnetization.

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Supporting Information Available: Synthetic procedure of complexes **1** and **2**, Figures of projection along the *c*-axis showing the tunnel-like backbone, projection along the *b*-axis showing the 3D network of **1**, XRD spectra for complexes **1** (calculated) and **2** (obs), IR spectra of **1** and **2**, temperature dependence of $\chi_M T$ and χ_M^{-1} for **2** measured at 10 kOe, real (χ') and imaginary (χ'') *ac* magnetic susceptibilities of **2** in zero applied *dc* field and an *ac* field of 2 Oe at different frequencies (111−1111 Hz), field dependence (0−50 kOe) of magnetization for **2** at 2.0 K, hysteresis loops at 1.8, 3.0, and 10 K for **2**, hysteresis loop at 5.0 K for **1** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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