

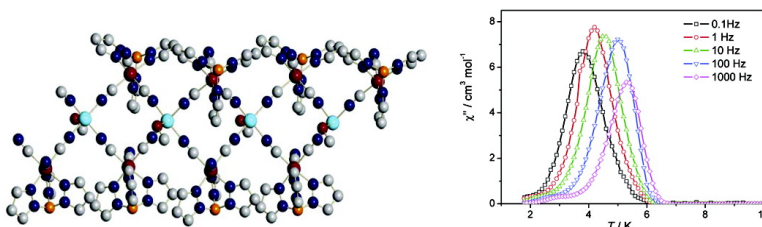
Communication

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The Observation of Superparamagnetic Behavior in Molecular Nanowires

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Single-chain magnets (SCMs) have attracted increasing interest because they exhibit the same slow magnetic relaxation as the single-molecule magnets (SMMs) with possible high magnetic transition temperature.¹ The possible synthetic strategies to achieve SCMs are using CN⁻ or N₃⁻ to bind the magnetic centers and the multidentate ligands as the protecting groups to separate one chain from the neighboring ones. The tailored cyanometalate precursor, (Bu₄N)[(Tp)Fe(CN)₃] **1**, has been chosen as our main building block. It was also reported by Julve's group as a tetraphenylphosphonium salt.² Tris(pyrazolyl)hydroborate (Tp) is a classical scorpionate ligand bearing a C₃ axis. Most recently it was used successfully as a protecting group at a heterometal site to prepare a topological analogue of the P cluster of nitrogenase.³ Compared to those precursors^{1c,4} reported before, Tp is sterically more demanding and bears a negative charge. Thus, it may direct the formation of isolated single chains. Herein, we report a new one-dimensional (1D) Ising cyano-bridged heterobimetallic chain, [(Tp)₂Fe^{III}₂(CN)₆Cu(CH₃OH)·2CH₃OH]_n **2**, which exhibits intrachain ferromagnetic coupling and superparamagnetic behavior.

A solution of (Bu₄N)[(Tp)Fe^{III}(CN)₃] in methanol was layered carefully on top of a solution of Cu(NO₃)₂·6H₂O in water. Brown, needlelike crystals of **2** were obtained after two weeks.

Single-crystal X-ray analysis of **2** reveals the formation of 1D chains of squares.⁵ The basic structural unit is a Cu₂(CN)₄Fe₂ square with each Cu^{II} shared by two adjacent squares (Figure 1). Within each square, the [(Tp)Fe(CN)₃]⁻ unit binds two Cu^{II} through two of its three cyanide groups. The iron atom has a distorted octahedral geometry, completed by three nitrogen atoms from a Tp ligand and three carbon atoms from cyanides. The Fe–C (cyano) bond length (1.911(4)–1.934(4) Å) is in good agreement with those observed in the low-spin iron (III) units.^{1c,2} The Fe–C–N angles for both terminal (175.9(4)–179.3(4)°) and bridging cyanides (174.5(3)–178.3(3)°) deviate from 180°. The copper atom is pentacoordinated, with a distorted square-pyramidal geometry. The basal positions are occupied by four cyanide nitrogen atoms, while the apical position is occupied by an oxygen from a methanol molecule. The Cu–N–C bond angles are 167.4(3)–179.3(3)°. The Cu–N bonds (average length 1.968(3) Å) are shorter than the Cu–O bond (2.232(3) Å). The average intrachain Cu···Fe, Cu···Cu and Fe···Fe separations are 5.018, 6.782, and 6.782 Å, respectively, whereas the shortest intermolecular Cu···Cu, Cu···Fe, and Fe···Fe distances are 11.100, 8.813, and 8.448 Å, respectively.

Magnetic measurements were performed on a sample of very thin, needlelike crystals of random directions in the temperature range of 1.8–300 K. The magnetic susceptibility data of **2** per

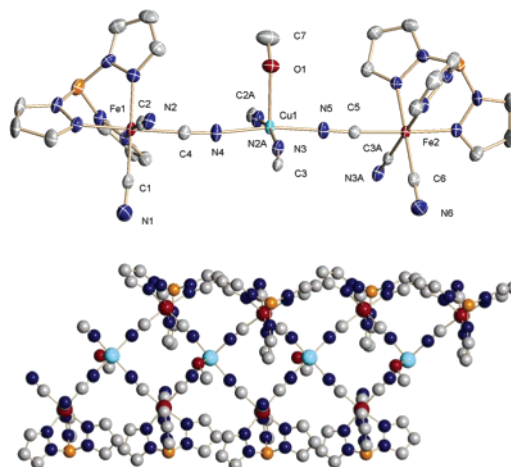


Figure 1. Structure of segments of the 1D chain of **2**. (Top) Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms and methanol molecules are omitted for clarity. (Bottom) 1D chain of square. Coloring scheme is the same as in the top drawing. Selected bond lengths [Å] and angles [deg]: Fe(1)–C(1) 1.920(4), Fe(1)–C(2) 1.933(4), Fe(1)–C(4), 1.911(4), Cu(1)–N(3) 1.968(3), Cu(1)–N(4) 1.952(3), Cu(1)–N(5) 1.965(3), Cu–N(2A)#1 1.988(3), Cu(1)–O(1) 2.232(3), Fe(1)–C(1)–N(1) 175.9(4), Fe(1)–C(2)–N(2) 174.5(3), Fe(1)–C(4)–N(4) 175.4(3), Fe(2)–C(5)–N(5) 175.3(3), Cu(1)–N(2A)–C(2A)#1 179.3(3), Cu(1)–N(3)–C(3) 167.4(3), Cu(1)–N(4)–C(4) 173.4(3), Cu(1)–N(5)–C(5) 176.2(3), N(4)–Cu(1)–N(3) 87.11(12), N(5)–Cu(1)–N(3) 90.77(12), O(1)–Cu(1)–N(5) 94.52(12), O(1)–Cu(1)–N(4) 94.91(12), O(1)–Cu(1)–N(3) 99.82(12). #1 = $x, -y + 5/2, z - 1/2$.

CuFe₂ unit (Figure S1) can be fitted by a Curie–Weiss law $\chi_M = C/(T - \theta)$ above 50 K, giving a Curie constant $C = 1.27 \text{ cm}^3 \text{ mol}^{-1}$ K and Weiss constant $\theta = +19.2$ K. The C value corresponds to two isolated low-spin Fe^{III} ($S = 1/2$) ions and one Cu^{II} ($S = 1/2$) ion, with $g = 2.12$. The positive value of θ indicates a ferromagnetic interaction between the Fe^{III} and Cu^{II} ions. The expression⁶ reported by E. Coronado et al. for the isolated double chain has been used to fit the data between 10–300 K. The obtained parameters are $J_1 = 32.3 \text{ cm}^{-1}$ (46.6 K), $J_2 = 12.3 \text{ cm}^{-1}$ (17.8 K), $g = 2.30$, $R = 7.5 \times 10^{-5}$ (where J_1 is magnetic interaction within the trimer; J_2 is magnetic interaction between adjacent trimers) (Figure S1). The ferromagnetic interaction between the Fe^{III} and Cu^{II} ions is due to the orthogonality of the magnetic orbitals of the low-spin Fe^{III} (d^5) and Cu^{II} (d^9) ions. As shown in Figure 2, a hysteresis loop is observed at 1.8 K with a coercive field of 120 Oe and a remnant magnetization of $0.86 \text{ N}\beta \text{ mol}^{-1}$, indicating a magnet-type behavior. Field-cooled magnetization (FCM) and zero-cooled magnetization (ZFCM) measurements under a field of 5 Oe, with a temperature step of 0.1 K, show the irreversibility below ca. 6 K, which is defined as the blocking temperature (Figure S2).

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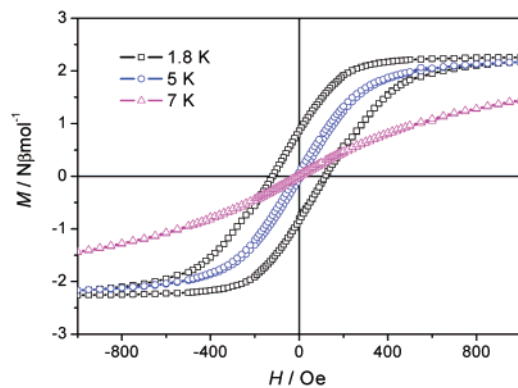


Figure 2. Hysteresis loop for **2** at 1.8 K.

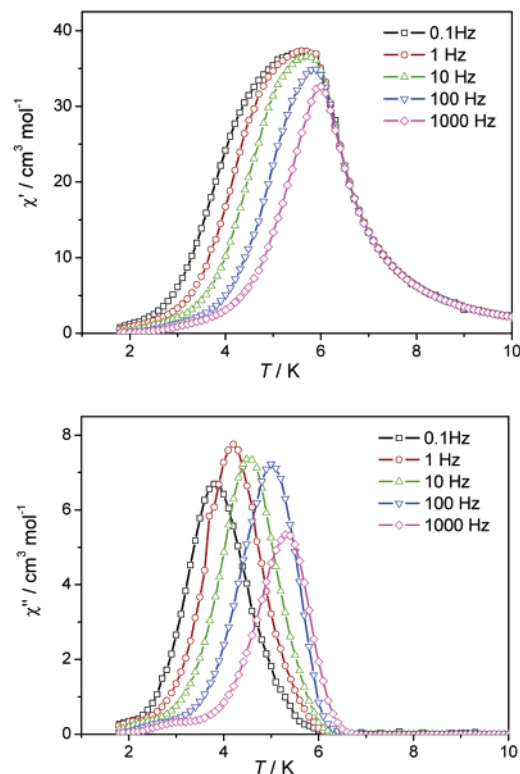


Figure 3. Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac susceptibility for **2** in zero applied static field with an oscillating field 5 Oe in frequency of 0.1–1000 Hz. The lines are guides.

To probe the dynamics of the magnetization relaxation of **2**, ac magnetic measurements were performed in a 5 Oe ac field oscillating at 0.1–1000 Hz. As shown in Figure 3, the in-phase susceptibility (χ') goes through a maximum, and the out-of-phase component (χ'') becomes different from zero also going through a maximum. They are strongly frequency-dependent below 6 K. The frequency dependence precludes a three-dimensional ordering. The shift of peak temperature (T_p) of χ'' is measured by a parameter $\phi = (\Delta T_p / T_p) / \Delta(\log f) = 0.10$, which is closer to a normal value for a superparamagnet.⁷ The ac oscillating frequency corresponding to the observed peaks at different temperatures is used as the relaxation rate ($1/\tau$) and an Arrhenius plot of $\ln(\tau)$ vs $1/T$ is given in Figure S3. The best set of parameters obtained is $\tau_0 = 2.8 \times 10^{-13}$ s and $\Delta/k_B = 112.3$ K, suggesting a thermally activated mechanism. The gap is comparable with the expected value

$\Delta_{\text{Glauber}}/k_B = 2J_{\text{eff}}' = 2 \times 46.6 = 93.2$ K based on Glauber's theory.^{8,1b} At a fixed temperature 5.05 K around the cusp of out-of-phase χ'' , a semicircle Cole–Cole plot is obtained (χ'' vs χ'), as shown in Figure S4. This can be fitted by a Debye model with $\alpha = 0.52$, indicating a distribution of relaxation time.⁹ The magnetic relaxation behavior is reminiscent of that observed in single-molecule magnets, as well as in molecular magnetic nanowires, where the energy barrier is originated from the magnetic anisotropy.^{1,10} In addition, the second harmonic ac susceptibilities shown in Figure S5 are negligibly small, essentially at a noise level. Absence of even harmonic response of χ' and χ'' excludes any spontaneous moment,¹¹ further supporting the low-dimensionality of **2**.

On the basis of crystallographic data, **2** is found to consist of well-isolated 1D $[\text{CuFe}_2]_n$ chains with a diameter of ca. 1.4 nm. The hysteresis and magnetic relaxation behaviors should be arise from the isolated ferromagnetic nanowires. In summary, both the crystal structure and magnetic studies support that this compound clearly shows a single-chain-magnet behavior. To the best of our knowledge, this is the first copper-containing case showing such a behavior. Further investigation on the new class of molecular magnetic nanowires with the versatile building block, $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$, is currently underway in our laboratory.

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Supporting Information Available: Details of synthesis and more magnetic data; X-ray structure data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Crystal data for $(\text{C}_{27}\text{H}_{32}\text{B}_2\text{CuFe}_2\text{N}_{18}\text{O}_3)$ (**2**): $M_r = 853.57$, $T = 213$ K, monoclinic, space group $P2_1/c$, $a = 15.0248(9)$ Å, $b = 19.0019(12)$ Å, $c = 13.4159(8)$ Å, $\beta = 100.55(10)^\circ$, $V = 3765.4(4)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.506$ g cm⁻³, $R1 = 0.0362$, $wR2 = 0.0796$ ($I > 2\sigma(I)$) for 21690 data (6620 independent), 490 parameters.
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