

Single-Molecule Magnets

 $[(\text{Tp})_8(\text{H}_2\text{O})_6\text{Cu}^{\text{II}}_6\text{Fe}^{\text{III}}_8(\text{CN})_{24}]^{4+}$: A Cyanide-Bridged Face-Centered-Cubic Cluster with Single-Molecule-Magnet Behavior**

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In the past decade, an increasing number of molecular clusters have been shown to exhibit magnetic bistability. These

species, called single-molecule magnets (SMMs), have gained considerable attention because they retain information in a single molecule rather than in a magnetic particle or array of particles^[1] and can potentially be used in quantum computers.^[2] Furthermore, understanding the magnetic properties of these molecules is important to help bridge the gap between the quantum and classical understanding of magnetism.^[3] The most thoroughly studied SMMs are $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ and its derivatives,^[4] but there are a number of other clusters containing Fe^{III} ,^[5] V^{III} ,^[6] Co^{II} ,^[7] or Ni^{II} ^[8] ions that have been reported to be SMMs. These species are all homometallic systems in which magnetic exchange interactions occur through bridging oxygen atoms.

Important to the future of the field of SMMs is the development of new synthetic schemes that can yield clusters with a large spin and/or anisotropy. Metal–cyanide cluster systems offer an advantage for achieving such control, through the substitution of various metal ions into a given structure type. Moreover, the nature of the magnetic exchange coupling between different metal ions in the resulting cluster is readily predicted.^[9] One approach to synthesizing high-nuclearity metal–cyanide clusters employs multidentate capping ligands to inhibit growth of an extended solid and direct the structure of the product. Many clusters have been prepared by this method,^[10–12] including the face-centered-cubic species $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$ ($\text{Me}_3\text{tacn} = N,N,N'$ -trimethyl-1,4,7-triazacyclononane)^[11b] and $[(\text{tach})_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Co}_8(\text{CN})_{24}\cdot\text{THF}]^{12+}$ ($\text{tach} = 1,3,5$ -triaminocyclohexane).^[11d] However, as far as we know, there are only a very few cyanide-bridged SMMs,^[13] and none of the established SMMs exhibit cubic symmetry.

In an effort to extend this chemistry, we have chosen to employ the precursor compound $(\text{Bu}_4\text{N})[(\text{Tp})\text{Fe}(\text{CN})_3]$ (**1**; $\text{Tp}^- = \text{hydrotris}(\text{pyrazolyl})\text{borate}$), featuring a low-spin Fe^{III} center octahedrally coordinated by three CN^- groups and the tridentate ligand Tp^- . This monoanionic complex has also been utilized by Julve and co-workers as the tetraphenylphosphonium salt.^[14] Tp^- is a classical scorpionate ligand with a C_3 axis, and in contrast to neutral capping ligands, such as Me_3tacn and tach , is negatively charged which should help alleviate the build-up of excessive positive charge in clusters. Thus, $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ is anticipated to direct the formation of new cyanide-bridged compounds with interesting structures and magnetic properties. Indeed, we have recently reported its use in the preparation of $[(\text{Tp})_2\text{Fe}_2(\text{CN})_6\text{Cu}(\text{CH}_3\text{OH})\cdot 2\text{CH}_3\text{OH}]_n$, a single-chain magnet with a blocking temperature of approximately 6 K.^[15] Herein, we disclose its use in the synthesis of $[(\text{Tp})_8(\text{H}_2\text{O})_6\text{Cu}^{\text{II}}_6\text{Fe}^{\text{III}}_8(\text{CN})_{24}]^{4+}$, a face-centered-cubic cluster exhibiting SMM-type behavior.

The compound $[(\text{Tp})_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}](\text{ClO}_4)_4\cdot 12\text{H}_2\text{O}\cdot 2\text{Et}_2\text{O}$ (**2**) crystallizes in space group $Im\bar{3}m$,^[16] with the well-isolated $[(\text{Tp})_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}]^{4+}$ molecules residing on special positions of mmm site symmetry. As shown in Figure 1, the clusters adopt a face-centered-cubic geometry, in which eight Tp^- -capped Fe^{III} ions are arranged in a cube and linked through cyanide to six Cu^{II} ions located just above the center of each cube face. Here, each octahedral $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ unit uses the three cyanide groups to connect with three Cu^{II} ions, which are further ligated by water to give

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[**] This work was supported by The Major State Basic Research Development Program (Grant No. G2000077500), the National Natural Science Foundation of China, and the US National Science Foundation (Grant No. CHE-0072691). H.C.Z. thanks the Research Corporation for a Research Innovation Award. The X-ray diffractometer was supported by NSF grant EAR-0003201. We thank Prof. Yi-Zhi Li and Dr. You Song for useful discussions and experimental assistance. $\text{Tp}^- = \text{hydrotris}(\text{pyrazolyl})\text{borate}$.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

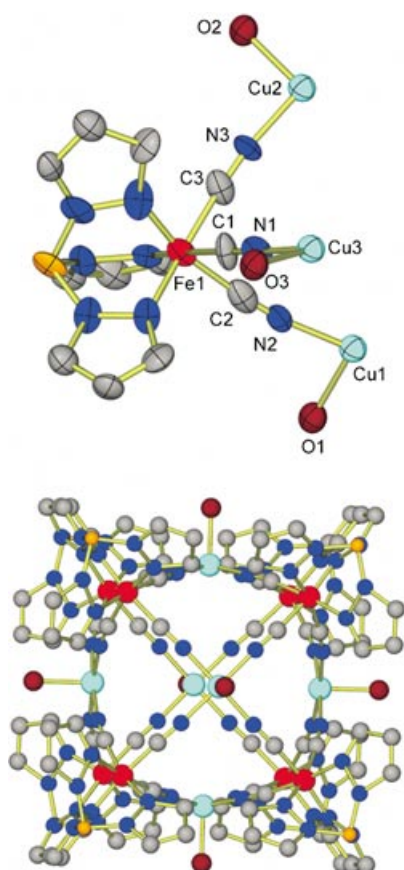


Figure 1. Structure of the face-centered-cubic cationic cluster in **2**. Top: repeat unit, thermal ellipsoids are set at 50% probability. Bottom: red Fe, turquoise Cu, orange B, gray C, blue N, dark red O; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1-C1 1.879(7), Fe1-C2 1.925(7), Fe1-C3 1.937(10), Cu1-N2 1.955(6), Cu2-N3 1.971(6), Cu3-N1 1.972(5), Cu1-O1 2.146(9), Cu2-O2 2.224(10), Cu3-O3 2.108(9); Fe1-C1-N1 173.6(6), Fe1-C2-N2 174.2(6), Fe1-C3-N3 174.6(7), Cu1-N2-C2 177.6(6), Cu2-N3-C3 171.3(6), Cu3-N1-C1 172.6(6), O1-Cu1-N2 99.59(17), O2-Cu2-N3 92.74(17), O3-Cu3-N1 97.68(15).

a square pyramidal $\{\text{Cu}(\text{NC})_4(\text{H}_2\text{O})\}$ coordination sphere. The Fe–C bond lengths (1.879(7)–1.937(10) Å) are in good agreement with those observed previously in related compounds.^[14,15] The Cu–N bonds range from 1.955(6) to 1.972(5) Å, and the Cu–O bonds vary from 2.108(9) to 2.224(10) Å. The O–Cu–N bond angles are 92.7(2)–99.6(2)°. All of the cyanide bridges deviate slightly from strict linearity, as reflected in the Fe–C–N and Cu–N–C angles, which are distributed within the range 171.3(6)–177.6(6)°. The $\text{C}\equiv\text{N}$ stretching region in the IR spectrum of **2** is consistent with the presence of only bridging cyanide ligands (a peak of medium intensity at 2176 cm^{-1}) and the high symmetry of the structure. In all, the cluster closely approaches cubic (O_h) symmetry, with Fe···Fe cube edge distances in the range 6.827–6.938 Å and crystallographically imposed Fe···Fe angles of 90°.

Importantly, the Cu_6Fe_8 cluster represents the first structurally characterized example of a face-centered-cubic cluster in which both metal sites are occupied by paramagnetic ions. Magnetic measurements were therefore per-

formed on a sample of pulverized single crystals of **2** in the temperature range of 1.8–300 K. The variation of $\chi_M T$ with temperature is plotted in Figure 2. At room temperature its value is 5.77 emu K mol^{-1} , somewhat above the spin-only

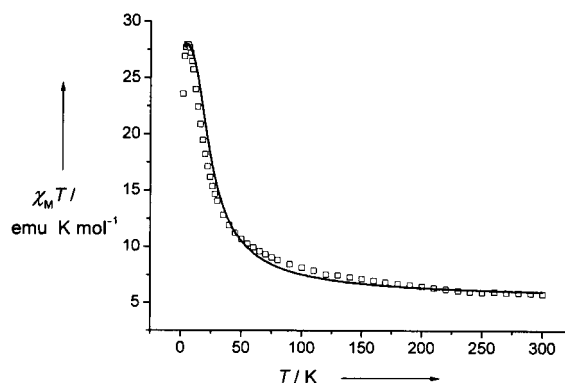


Figure 2. Temperature dependence of $\chi_M T$ for compound **2**, as measured in an applied DC field of 2000 G. The solid line corresponds to a simulation of the data with $J = 15 \text{ cm}^{-1}$, $g = 2.00$, and temperature-independent paramagnetism (TIP) = 0.00070 emu mol^{-1} .

value of 5.25 emu K mol^{-1} expected for eight low-spin Fe^{III} ($S = 1/2$) and six Cu^{II} ($S = 1/2$) ions in the absence of any exchange coupling. With decreasing temperature, $\chi_M T$ increases, reaching a maximum of 27.94 emu K mol^{-1} at approximately 5 K, after which point it decreases to 23.57 emu K mol^{-1} at 1.8 K. This magnetic behavior is indicative of the expected ferromagnetic interactions between the orthogonal spin orbitals of the Fe^{III} and Cu^{II} ions,^[9] resulting in an $S = 7$ ground state. This conclusion is confirmed by the field dependence of the magnetization of **2** at 1.8 K, which saturates at a value of $M_S = 13.78 N\mu_B$ (see the Supporting Information). The sudden decrease in $\chi_M T$ below 5 K is attributed to the presence of zero-field splitting, the effects of which are also discernible in the magnetization data shown in Figure 3. The $\chi_M T$ data above 5 K were simulated employing

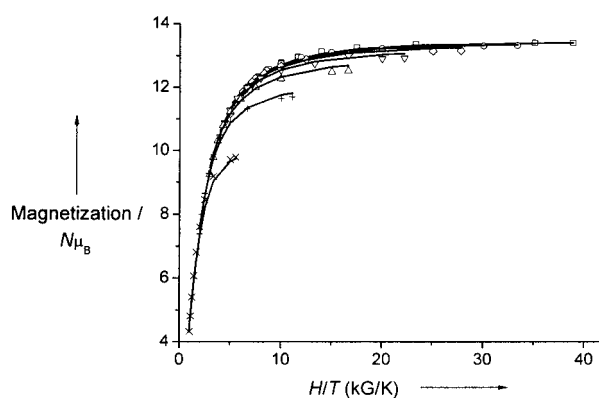


Figure 3. Plot of reduced magnetization, $M/N\mu_B$ (N is Avogadro's number and μ_B is Bohr magneton) versus H/T for **2**. Data were measured in the 1.8–10 K range and at seven magnetic fields: (x) 10.0, (+) 20.0, (Δ) 30.0, (∇) 40.0, (\diamond) 50.0, (\circ) 60.0, and (\square) 70.0 kG. The solid lines resulted from least-squares fitting of the data in the 1.8–10 K range; see text for fitting parameters.

MAGPAK^[17] and an exchange Hamiltonian of the form given in Equation (1).

$$\begin{aligned} \hat{H} = & -2J[\hat{S}_{\text{Fe}1} \cdot (\hat{S}_{\text{Cu}1} + \hat{S}_{\text{Cu}2} + \hat{S}_{\text{Cu}3}) + \hat{S}_{\text{Fe}2} \cdot (\hat{S}_{\text{Cu}1} + \hat{S}_{\text{Cu}3} + \hat{S}_{\text{Cu}4}) + \\ & \hat{S}_{\text{Fe}3} \cdot (\hat{S}_{\text{Cu}1} + \hat{S}_{\text{Cu}4} + \hat{S}_{\text{Cu}5}) + \hat{S}_{\text{Fe}4} \cdot (\hat{S}_{\text{Cu}1} + \hat{S}_{\text{Cu}2} + \hat{S}_{\text{Cu}5}) + \\ & \hat{S}_{\text{Fe}5} \cdot (\hat{S}_{\text{Cu}6} + \hat{S}_{\text{Cu}2} + \hat{S}_{\text{Cu}3}) + \hat{S}_{\text{Fe}6} \cdot (\hat{S}_{\text{Cu}6} + \hat{S}_{\text{Cu}3} + \hat{S}_{\text{Cu}4}) + \\ & \hat{S}_{\text{Fe}7} \cdot (\hat{S}_{\text{Cu}6} + \hat{S}_{\text{Cu}4} + \hat{S}_{\text{Cu}5}) + \hat{S}_{\text{Fe}8} \cdot (\hat{S}_{\text{Cu}6} + \hat{S}_{\text{Cu}2} + \hat{S}_{\text{Cu}5})] \end{aligned} \quad (1)$$

The best simulation was obtained with $J = +15 \text{ cm}^{-1}$, which indicates significantly stronger coupling than previously observed for complexes containing more bent Fe^{III} -CN- Cu^{II} bridges.^[18]

To assess the zero-field splitting associated with the $S = 7$ ground state, magnetization data were collected on compound **2** at a variety of fields in the temperature range 1.8–10 K (see Figure 3). The seven isofield data sets were fitted using ANISOFIT^[11c] to give zero-field splitting parameters of $D = -0.16 \text{ cm}^{-1}$ and $E = 0.0055 \text{ cm}^{-1}$ with $g = 1.93$. Thus, despite the near cubic symmetry of the cluster, the presence of orbitally degenerate low-spin Fe^{III} centers enables the development of significant axial magnetic anisotropy. Indeed, if the sign and magnitude of D obtained from the fit are correct, then the Cu_6Fe_8 cluster should behave as an SMM with a spin reversal barrier of $U = S^2 |D| = 7.8 \text{ cm}^{-1}$.

One of the defining characteristics of an SMM is the observation of a frequency-dependent out-of-phase AC magnetic susceptibility (χ_M'') signal. To determine whether the slow magnetization relaxation behavior occurs in **2**, AC magnetic measurements were performed in the temperature range of 1.8–6 K (Figure 4). Although no maximum was

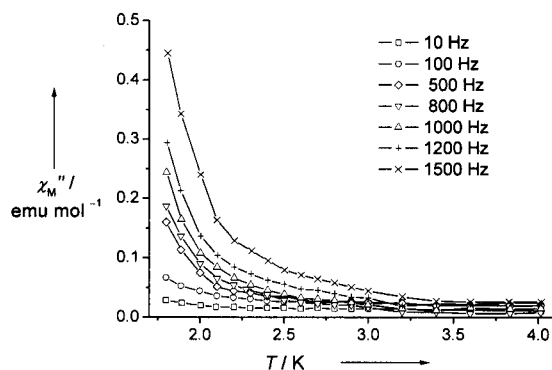


Figure 4. Temperature dependence of the out-of-phase component of the AC susceptibility for **2** in zero applied static field and with a 5 G field oscillating at frequencies between of 10 and 1500 Hz. The lines are to guide the eye.

observed down to 1.8 K, frequency-dependent χ_M'' signals were observed below 3 K, which indicates the superparamagnet-like slow relaxation of an SMM. The results are similar to those observed for [(tmphen) $\text{Mn}_5(\text{CN})_{12}$] (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline),^[13b] and place an upper bound of 20 cm^{-1} (assuming an attempt frequency of $1/\tau_0 < 10^{10} \text{ Hz}$) on the effective spin-reversal barrier for the Cu_6Fe_8 cluster.

In summary, the use of Tp^- as a capping ligand has permitted isolation of a face-centered-cubic cluster, with a

well-isolated $S = 7$ ground state. Despite its cubic symmetry, the molecule possesses substantial axial magnetic anisotropy ($D = -0.16 \text{ cm}^{-1}$), which leads to single-molecule-magnet behavior.

Experimental Section

1: Prepared by a modified literature method.^[14] **2:** Solid $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37 mg, 0.13 mmol) was added to a solution of $(\text{Bu}_4\text{N})[(\text{Tp})\text{Fe}(\text{CN})_3]$ (59 mg, 0.10 mmol) in acetonitrile and ethanol (5 mL; mole ratio = 2:1). The solution was filtered. Brown block-shaped crystals of **2** were obtained in 85% yield by diffusing diethyl ether vapor into the filtrate. IR: $\nu = 2176 \text{ cm}^{-1} (\nu_{\text{CN}})$; elemental analysis (%) calcd for $\text{C}_{96}\text{H}_{116}\text{B}_8\text{Cl}_4\text{Cu}_6\text{Fe}_8\text{N}_{72}\text{O}_{34}$: C 29.73, H 3.01, N 26.00; found: C 30.02, H 2.73, N 26.24.

Received: August 3, 2004

Keywords: cluster compounds · cyanides · iron · magnetic properties · single-molecule magnets

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- [16] Crystallographic analysis: **2** (C₁₀₄H₁₃₆B₈Cl₄Cu₆Fe₈N₇₂O₃₆): $M_r = 4027.17$, $T = 213$ K, orthorhombic, space group *Immm*, $a = 16.2010(16)$, $b = 35.317(4)$, $c = 17.1566(17)$ Å, $V = 9816.5(18)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.362$ g cm⁻³, $R_1 = 0.0621$, $wR_2 = 0.1363$ ($I > 2\sigma(I)$) for 23664 data (3882 independent), 470 parameters, and 15 restraints. Data were collected on a Bruker Apex CCD diffractometer. Absorption corrections were applied for **2** using SADABS supplied by Bruker. The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXTL-97. In the structure of **2**, all the atoms of the Tp ligands and some hydrogen atoms are disordered. CCDC-246475 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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