

Symmetry-Based Magnetic Anisotropy in the Trigonal Bipyramidal Cluster $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_2(\text{CN})_6]^{4+}$

Cai-Feng Wang, Jing-Lin Zuo,* Bart M. Bartlett, You Song, Jeffrey R. Long,* and Xiao-Zeng You

Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China, and Department of Chemistry, University of California, Berkeley, California 94270-1460

Received March 15, 2006; E-mail: zuojl@nju.edu.cn; jrlong@berkeley.edu

For more than a decade, it has been recognized that molecules possessing a high-spin ground state, S , and a negative uniaxial anisotropy, D , can exhibit slow magnetic relaxation at low temperatures.¹ Such “single-molecule magnets” have received considerable attention, owing in part to the possibility that they might, one day, find applications in high-density information storage, quantum computing, or spin-based molecular electronics.² Since any of these potential applications would benefit from the use of molecules with higher blocking temperatures than currently known,³ the development of synthetic methods for producing high-spin, high-anisotropy molecules has become a major research focus.

While much of this research has been directed toward transition metal–oxo clusters,^{1,3,4} some success has also been achieved with use of cyanide as a bridging ligand.⁵ Here, organic blocking ligands can be utilized to direct the assembly of specific structures, wherein variation of the metal ions can provide adjustability to both spin state and magnetic anisotropy. Recently, we showed that the incorporation of low-spin iron(III) centers into the face-centered cubic cluster $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}]^{4+}$ led to single-molecule magnet behavior, despite the apparent O_h symmetry of its core structure.⁶ We now demonstrate that employing a tridentate blocking ligand on the Cu^{II} centers in this system generates a trigonal bipyramidal cluster, $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_2(\text{CN})_6]^{4+}$, in which the reduced symmetry affords a significantly increased anisotropy barrier.

Synthesis of the new cluster proceeds via reaction of $[(\text{Me}_3\text{tacn})\text{Cu}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane)⁷ with $(\text{Bu}_4\text{N})[\text{TpFe}(\text{CN})_3]$ ($\text{Tp}^- = \text{hydrotris}(\text{pyrazolyl})\text{-borate}$)⁸ in a mixture of ethanol and acetonitrile. Diffusion of diethyl ether vapor into the resulting solution affords dark brown block-shaped crystals of $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_2(\text{CN})_6](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (**1**) in 82% yield.⁹

The crystal structure of **1** features the pentanuclear $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_2(\text{CN})_6]^{4+}$ cluster depicted in Figure 1. Here, two opposing $[\text{TpFe}(\text{CN})_3]^-$ complexes are connected via a triangle of three $[(\text{Me}_3\text{tacn})\text{Cu}]^{2+}$ units to give a trigonal bipyramidal metal–cyanide core with approximate D_{3h} symmetry. We note that this core geometry has been obtained previously with other metals and different capping ligands.^{5b,e} The cyanide bridges connecting metal centers in **1** are quite close to linearity, with $\text{Fe}-\text{C}\equiv\text{N}$ and $\text{Cu}-\text{N}\equiv\text{C}$ angles falling in the range $168.1(2)$ – $178.6(3)^\circ$. The coordination at each Cu^{II} center is square pyramidal, with the cyanide nitrogen atoms lying in the basal plane. The $\text{Fe}-\text{C}$ bond distances range from 1.911(3) to 1.938(3) Å, in good agreement with those observed previously for structures containing $[\text{TpFe}(\text{CN})_3]^-$.^{6,8} Importantly, the local three-fold symmetry axes associated with the coordination environments of the two low-spin Fe^{III} centers are roughly collinear, such that one might expect the anisotropy stemming from orbital angular momentum to be maximized.¹⁰ Within the crystal structure, the closest contacts between metal

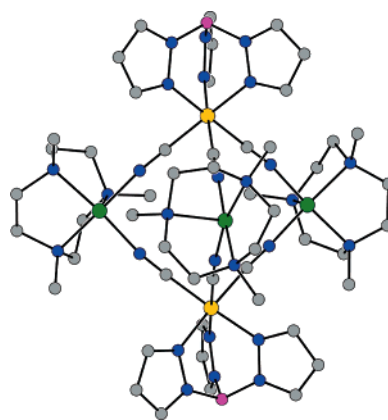


Figure 1. Structure of the trigonal bipyramidal cluster $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_2(\text{CN})_6]^{4+}$ in **1**. Orange, green, magenta, gray, and blue spheres represent Fe, Cu, B, C, and N atoms, respectively; H atoms are omitted for clarity. Selected mean interatomic distances (Å) and angles (deg): $\text{Fe}-\text{C}$ 1.926(9), $\text{Fe}-\text{N}$ 1.96(1), $\text{Cu}-\text{N}_{\text{CN}}$ 1.98(1), $\text{Cu}-\text{N}_{\text{tacn}}$ 2.10(7), $\text{C}\equiv\text{N}$ 1.133(9), $\text{Fe}\cdots\text{Cu}$ 5.02(3), $\text{Cu}\cdots\text{Cu}$ 6.7(2), $\text{Fe}-\text{C}\equiv\text{N}$ 177(1), $\text{Cu}-\text{N}\equiv\text{C}$ 172(3), $\text{C}-\text{Fe}-\text{C}$ 88(2), $\text{C}-\text{Fe}-\text{N}$ 92(2), $\text{N}-\text{Fe}-\text{N}$ 89.0(8), $\text{N}_{\text{CN}}-\text{Cu}-\text{N}_{\text{CN}}$ 88(2), $\text{N}_{\text{CN}}-\text{Cu}-\text{N}_{\text{tacn}}$ 97(5), $\text{N}_{\text{tacn}}-\text{Cu}-\text{N}_{\text{tacn}}$ 84.5(7).

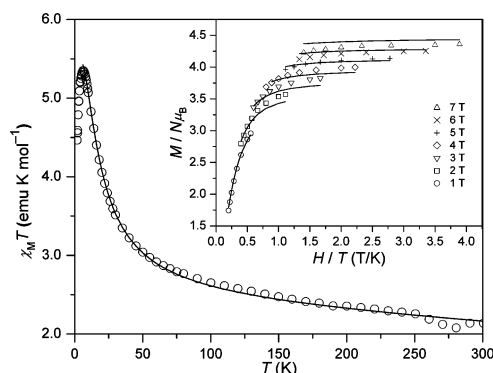


Figure 2. dc magnetic susceptibility of **1** recorded under a 2 kOe measuring field. Inset: Reduced magnetization data for **1** at low temperatures. Solid lines represent fits to the data (see text for details).

centers in neighboring clusters are 8.43 Å, with no intervening hydrogen-bonding pathways. Thus, we can anticipate that the magnetic properties observed above 1.8 K will be mainly those of the isolated cluster units.

dc magnetic susceptibility measurements were performed on a polycrystalline sample of **1** at 2 kOe in the temperature range 1.8–300 K (see Figure 2). At room temperature, the compound exhibits $\chi_M T = 2.14 \text{ emu}\cdot\text{K}/\text{mol}$, which is higher than the value of 1.875 $\text{emu}\cdot\text{K}/\text{mol}$ expected for a spin-only contribution from two low-spin Fe^{III} ($S = 1/2$) and three Cu^{II} ($S = 1/2$) ions in the absence of any exchange coupling. As the temperature is lowered, $\chi_M T$ rises to a maximum of 5.35 $\text{emu}\cdot\text{K}/\text{mol}$ at 6.0 K.

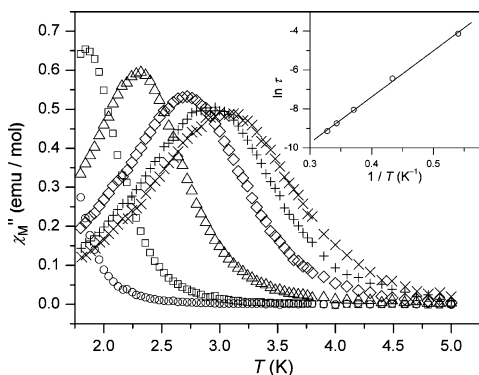


Figure 3. Out-of-phase component of the ac magnetic susceptibility data for **1**, recorded with switching frequencies of 1 (○), 10 (□), 100 (△), 499 (◇), 997 (+), and 1488 (×) Hz. Inset: Arrhenius law fit of peak maximum as a function of relaxation time.

This behavior typifies ferromagnetic coupling between the orthogonal spin orbitals of octahedral Fe^{III} (t_{2g}) and square pyramidal Cu^{II} (b_{1g}) centers, resulting in an $S = 5/2$ ground state. Below 6 K, $\chi_M T$ decreases, suggesting the presence of significant zero-field splitting in the ground state. Note that the observation that $\chi_M T$ is independent of field strength for applied fields below 2 kOe (see Figure S1) precludes the presence of significant intermolecular interactions. Fitting the 2 kOe $\chi_M T$ data using the isotropic spin Hamiltonian $\hat{H} = -2J(\hat{S}_{Fe(1)} + \hat{S}_{Fe(2)}) \cdot (\hat{S}_{Cu(1)} + \hat{S}_{Cu(2)} + \hat{S}_{Cu(3)})$, which includes only nearest-neighbor exchange, gave $g = 2.245(4)$, $J = 8.5(1) \text{ cm}^{-1}$, and $TIP = -1.0 \times 10^{-3} \text{ emu/mol}$ ($R = 1.2 \times 10^{-3}$). The large Landé splitting can be ascribed to a combination of the orbital contributions from the low-spin Fe^{III} centers¹¹ and individual factors of >2 associated with the Cu^{II} centers. The magnitude of the exchange coupling is somewhat lower than the 15 cm^{-1} estimated for $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}]^{4+}$,⁶ but slightly greater than the 5 or 6 cm^{-1} observed for other molecules with Fe^{III}–CN–Cu^{II} linkages.¹²

The magnetization data collected for **1** at temperatures between 1.8 and 5 K are also consistent with an $S = 5/2$ ground state (see inset in Figure 2). Here, the non-superposition of the isofield lines confirms the presence of significant zero-field splitting. Fitting the data using ANISOFIT 2.0¹³ afforded zero-field splitting parameters of $D = -5.7 \text{ cm}^{-1}$ and $E = 1.4 \times 10^{-3} \text{ cm}^{-1}$, with $g = 2.53$. Importantly, the axial anisotropy is much greater than that associated with the $S = 7$ ground state of the face-centered cubic cluster $[\text{Tp}_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}]^{4+}$, for which $D = -0.16 \text{ cm}^{-1}$.⁶ This difference likely arises due to the lower core symmetry of the molecule, which does not lead to near-cancellation of individual ion anisotropy terms. Based on the observed values of S and D , $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_2(\text{CN})_6]^{4+}$ should be a single-molecule magnet with a spin reversal barrier of $U = (S^2 - 1/4)|D| = 34 \text{ cm}^{-1}$.

As shown in Figure 3, the low-temperature ac susceptibility data obtained for **1** are indeed indicative of single-molecule magnet behavior. The χ_M'' values for a given frequency attain a maximum that shifts to lower temperature upon decreasing the frequency. The χ_M'' peak positions were determined using fits to Lorentzian lines, and the plot of $\ln \tau$ versus $1/T$ (see inset) follows the Arrhenius expression $\ln \tau = U_{\text{eff}}/k_B T + \ln \tau_0$. Least-squares fitting gave $\tau_0 = 4.8 \times 10^{-8} \text{ s}$ and an effective spin-reversal barrier of $U_{\text{eff}} = 16 \text{ cm}^{-1}$. The reduction by roughly 50% in the observed barrier height may be attributable to the usual thermally activated tunneling mechanism.

The foregoing results demonstrate the enormous impact that cluster symmetry can have on magnetic anisotropy, with a ligand-induced switch from a cubic to a linear arrangement of Fe^{III} centers

leading to significant enhancement of the anisotropy barrier. Of particular import is the observation that the resulting barrier is substantial despite the ground-state spin being just $S = 5/2$. Future efforts will therefore focus on assembly of linear vertex-sharing trigonal bipyramidal oligomers of the type $[\text{Tp}_2(\text{Me}_3\text{tacn})_3\text{Cu}_3\text{Fe}_{n+1}(\text{CN})_{6n}]^{(3n+1)+}$ ($n = 2, 3, 4, \dots$; $S = (4n+1)/2$) via three-component reactions incorporating $[\text{Fe}(\text{CN})_6]^{3-}$.

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Supporting Information Available: Experimental details and additional magnetic characterization data (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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