J|A|C|S
COMMUNICATIONS

Exchange-Biased Dimers of Single-Molecule Magnets in OFF and ON States

Rashmi Bagai,† Wolfgang Wernsdorfer,‡ Khalil A. Abboud,† and George Christou*,†

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and Institut Néel-CNRS, 38042 Grenoble, Cedex 9, France

Received July 18, 2007; E-mail: christou@chem.ufl.edu

Single-molecule magnets (SMMs) are molecules that possess a significant barrier (vs kT) to reorientation of their magnetization (magnetic moment) vector as a result of the combination of a large ground state spin (S) and Ising (easy axis) magnetoanisotropy (negative axial zero-field splitting parameter (D)).[1] As such, they represent a molecular (bottom-up) approach to nanomagnetism. They also straddle the classical/quantum interface by displaying not just classical magnetization hysteresis but also quantum tunneling of magnetization (QTM)[2] and quantum phase interference.[3] For all these reasons, they have been proposed as potential qubits for quantum computation.[4] In this regard, the report of supramolecular hydrogen-bonded pairs of $[Mn_4O_3Cl_4(O_2CEt)_3(py)_3]$ ($[Mn_4]_2$; py = pyridine) SMMs was an important development. A weak intradimer antiferromagnetic exchange interaction coupled the two halves of $[Mn_4]_2$ and provided an exchange-bias that shifted the QTM positions away from zero field for the first time.[5] Subsequent EPR and magnetization studies established that the two connected SMMs of $[Mn_4]_2$ are entangled and in quantum superposition states.[6,7] The next hurdle to the potential use of dimers as two-qubit systems is how to have the exchange-bias OFF and ON; $[Mn_4]_2$ is not amenable to removal of the intradimer H-bonds. The present work reveals one way that such a two-state system could be developed by showing how an $[Fe_9]_2$ supramolecular dimer of SMMs can be in OFF and ON exchange-coupled states mediated by a single H-bond.

We are investigating the use of *N*,*N*′-bis(2-hydroxyethyl)-ethylenediamine (heenH$_2$) as a new O,N,N,O-based chelate in cluster chemistry. Such chelates with multiple alcohol arms often have one arm remaining protonated and not bound to a metal,[8] and we have been looking for cases where this leads to intermolecular hydrogen-bonded pairs of SMMs such as in $[Mn_4]_2$. This has now been found to be the case for the $FeCl_3/NaO_2CPh/heenH_2$ (1:2:1) reaction in MeCN, which gave well-formed crystals of $[Fe_9O_4(OH)_4(O_2CPh)_{13}(heenH)_2]$ (**1**) as **1**·9MeCN in 15% nonoptimized yield. The structure[9] consists of pairs of Fe$_9$ clusters arranged as head-to-head dimers. Each Fe$_9$ contains two $[Fe_4(\mu_3\text{-}O)(\mu_3\text{-}OH)]^{9+}$ butterfly like subunits (Fe1, Fe5, Fe6, Fe7, O5, O27 and Fe4, Fe7, Fe8, Fe9, O21, O31) fused at body atom Fe7 (Figure 1), and attached to two additional Fe atoms Fe2 and Fe3 by two μ_3-OH$^-$ (O6 and O11) and two μ_3-O^{2-} ions (O7 and O14). There are thirteen PhCO$_2^-$ groups, nine η^1:η^1:μ-bridging and four η^1-terminal on Fe1, Fe4, Fe6, and Fe8, with their noncoordinated O atom intramolecularly H-bonded to OH$^-$ ions (O6, O11, O5, and O21, respectively). Each heenH$^-$ is a tridentate chelate to an Fe atom (Fe5 and Fe9) and bridges through its deprotonated arm to a neighboring Fe atom. Each remaining heenH$^-$ protonated arm (O30 and O38) is unbound and hydrogen-bonding. The one on Fe9 forms an intramolecular H-bond to benzoate O atom O32 (O38···O32 = 2.788 Å) with no disorder. The one on Fe5, however, is disordered, forming intramolecular H-bonds to benzoate O atom O28 (O30···O28 = 2.882 Å) or to the same heenH$^-$ arm of the corresponding chelate on the neighboring Fe9 molecule (O30···O39 = 2.753 Å) (Figure 2). Refinement of the disorder components gave an essentially statistical 36:64% mixture of the intra- and intermolecular H-bonding situations, since there are two equivalent forms of the latter (Figure 2). Thus, $^2/_3$ of the molecules in the crystal are linked within H-bonded $[Fe_9]_2$ dimers, whereas the other third are within non-H-bonded dimers.

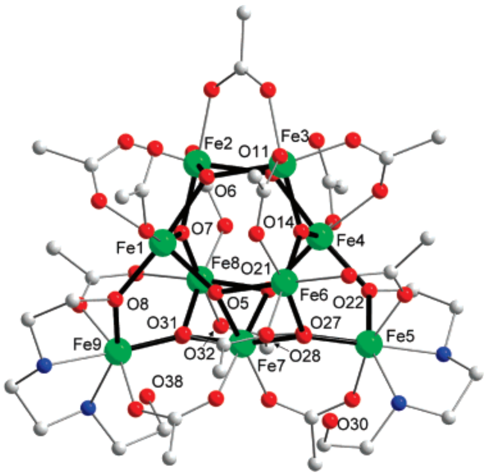

Figure 1. Molecular structure of complex **1** with only the ipso C atoms of benzoate rings shown for clarity. The core is outlined in bold. Color code: Fe, green; O, red; N, blue; C, gray.

Variable-temperature magnetic susceptibility data (χ_M) were collected on dried **1** restrained in eicosane in a 0.1 T dc field and 5.0−300 K temperature range. $\chi_M T$ gradually decreases from 13.35 cm^3 K mol^{-1} at 300 K to 11.65 cm^3 K mol^{-1} at 150 K, stays essentially constant until 60 K and then decreases to 8.73 cm^3 K mol^{-1} at 5.0 K, indicating predominantly antiferromagnetic interactions and an $S = {}^7/_2$ ground state.[10] The latter was confirmed by fits of dc magnetization data collected in the 1.8−10 K and 0.1−4 T ranges, which gave $S = {}^7/_2$, $D = -0.85(1)$ cm^{-1} and $g = 2.0(1)$.[10] Ac susceptibility data were collected in the 1.8−10 K range under a 3.5 G ac field oscillating at 50−1000 Hz. The in-phase $\chi_M' T$ decreases with decreasing T before exhibiting a frequency-dependent drop below ~3 K.[10] Extrapolation from above 3 to 0 K gives a value of ~7.9 cm^3 Kmol^{-1}, confirming an $S = {}^7/_2$ ground state. The drop below ~3 K and the concomitant frequency-dependent out-of-phase (χ_M'') signal suggest **1** to possibly be a SMM. To investigate this possibility, magnetization vs dc field scans were carried out on single crystals of **1**·9MeCN using a micro-SQUID apparatus.[11] Hysteresis loops were indeed observed, whose coercivity increases with decreasing T (Figure 3) and increasing scan rate,[10] confirming complex **1** to be a SMM.

---

† University of Florida.
‡ Institut Néel-CNRS.

10.1021/ja075382o CCC: $37.00 © 2007 American Chemical Society

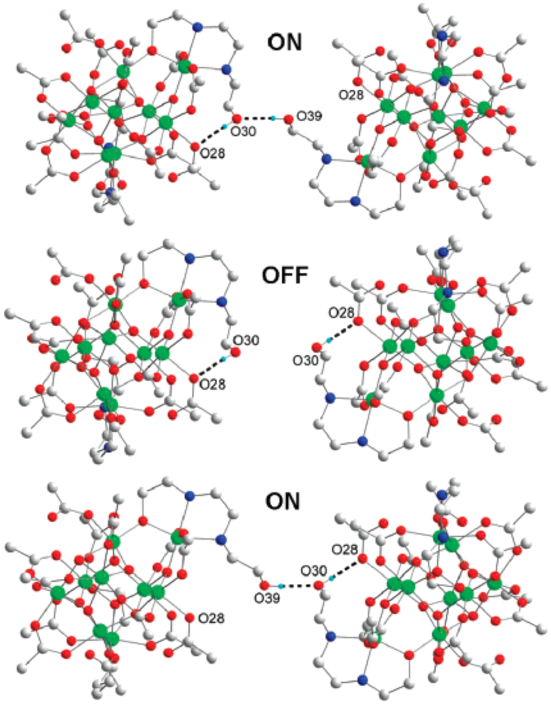

Figure 2. The $[Fe_9]_2$ dimer showing intermolecular (top, bottom) or only intramolecular (middle) O−H⋯O hydrogen-bonding, and the resultant ON or OFF state with respect to the coupling of the two molecules. Color code: Fe, green; O, red; N, blue; C, gray; H, sky blue.

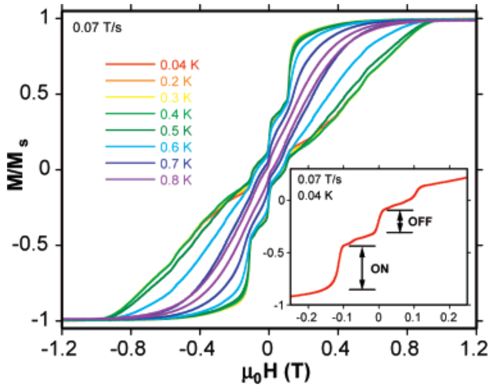

Figure 3. Magnetization (*M*) vs dc field (*H*) hysteresis loops for **1**·9MeCN at the indicated temperatures and field scan rate. The inset shows the assignment of the 0 and 0.11 T steps.

QTM steps were observed, the first appearing before zero-field as expected for an exchange-bias effect from the neighbor within the $[Fe_9]_2$ dimer, and as seen for $[Mn_4]_2$.[5] However, a QTM step at zero field was also seen, and this is not expected for an exchange-biased dimer. However, this and the ~2:1 ratio of the steps at 0.11 and 0.0 T can be explained with reference to Figure 2 as due to an antiferromagnetic exchange interaction between the two Fe_9 units mediated by the intermolecular H-bond. Thus, 64% of the $[Fe_9]_2$ dimers show an exchange-bias (ON), whereas the remaining 36% do not (OFF). The spin Hamiltonian ($\mathscr{H}_i$) for each Fe_9 SMM with Ising-like anisotropy is given by

$$\mathscr{H}_i = D\hat{S}_{zi}^{\ 2} + g\mu_B\mu_0 S_i\cdot H \tag{1}$$

where $i = 1$ or 2 (the two Fe_9 SMMs of the dimer), D is the axial anisotropy constant, μ_B is the Bohr magneton, μ_0 is the vacuum permeability, and H is the applied field. The second term in eq 1 is the Zeeman energy. The Hamiltonian ($\mathscr{H}$) for the $[Fe_9]_2$ dimer is then given by

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2 - 2J'\hat{S}_1\cdot\hat{S}_2 \tag{2}$$

From the $H_{ex} = 0.11$ T (H_{ex} = exchange-bias field) and the relationship $J' = -g\mu_B H_{ex}/(2S)$ ($\mathscr{H} = -2J'S_i\cdot S_j$ convention)[12] can be calculated that the intermolecular interaction is $J' = -0.04$ K, that is, very weakly antiferromagnetic.

Thus, 64% of the dimers in the crystal are in an ON state and 36% are OFF (Figure 2). Since the intermolecular interaction J' will serve to quantum mechanically entangle the two molecules and generate superposition states,[5−7] the ON and OFF states with respect to the interaction thus correspond to potential ON and OFF states of a coupled two-qubit system for quantum computation. Being able to have the interaction ON or OFF in some simple way is important, and the present work shows that a superexchange pathway via a single H-bond will suffice. Note that the $[Fe_9]_2$ head-to-head dimer structure does not depend on the intermolecular H-bond, unlike $[Mn_4]_2$ where a total of six equivalent C−H⋯Cl intermolecular H-bonds clearly control the crystallization of the dimer. Of course, the next important hurdle is now to devise a means to switch an exchange-biased dimer of SMMs from ON to OFF, and vice-versa, in a deliberate manner, and such investigations are currently in progress.

Acknowledgment. We thank NSF (Grant CHE-0414555) for support.

Supporting Information Available: Crystallographic details for **1**·9MeCN in CIF format and dc and ac magnetism data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66.
(2) Novak, M. A.; Sessoli, R. In *Quantum Tunneling of Magnetization-QTM'94*; Gunther, L.; Barbara, B., Eds.; NATO ASI Series E; Kluwer: London, 1995; Vol. 301, pp 171−188. Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett*. **1996**, *76*, 3830.
(3) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133.
(4) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789.
(5) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406.
(6) Hill, S.; Edwards, R. S.; Aliaga-Alcalde, N.; Christou, G. *Science* **2003**, *302*, 1015.
(7) Tiron, R.; Wernsdorfer, W.; Foguet-Albiol, D.; Aliaga-Alcalde, N.; Christou, G. *Phys. Rev. Lett*. **2003**, *91*, 227203(1−4).
(8) Brechin, E. K.; Yoo, J.; Nakano, M.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Chem. Commun.* **1999**, 783.
(9) Crystal data for **1**·9MeCN: $C_{121}H_{126}N_{13}Fe_9O_{38}$, M = 2873.02, triclinic, $P\bar{1}$, $a = 17.0412(15)$ Å, $b = 19.8622(16)$ Å, $c = 19.9519(17)$ Å, $\alpha = 89.227(2)°$, $\beta = 77.146(2)°$, $\gamma = 77.433(2)°$, $V = 6421.9(9)$ Å^3, $Z = 2$, $T = 173(2)$ K, Final $R_1 = 7.4\%$ and $wR_2 = 18.01\%$.
(10) See Supporting Information.
(11) Wernsdorfer, W. *Adv. Chem. Phys*. **2001**, *118*, 99.
(12) Tiron, R.; Wernsdorfer, W.; Aliaga-Alcalde, N.; Christou, G. *Phys. Rev. B*, **2003**, *68*, 140407(1−4).

JA075382O