

## A Redox-Switchable Single-Molecule Magnet Incorporating $[\text{Re}(\text{CN})_7]^{3-}$

Danna E. Freedman, David M. Jenkins, Anthony T. Iavarone, and Jeffrey R. Long\*

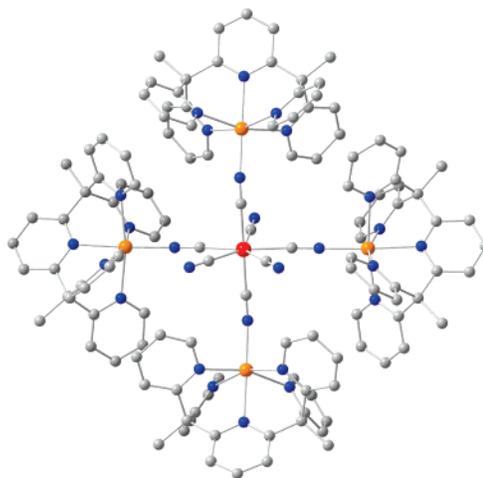
Department of Chemistry, University of California, Berkeley, California 94720-1460

Received September 29, 2007; E-mail: jrlong@berkeley.edu

A variety of transition metal-oxo clusters have now been shown to exhibit slow magnetic relaxation at low temperatures.<sup>1</sup> Such “single-molecule magnets” possess a high spin ground state,  $S$ , and an axial zero-field splitting,  $D < 0$ , which combine to give a relaxation barrier of  $U = S^2|D|$  if  $S$  is an integer or  $U = (S^2 - 1/4)|D|$  if  $S$  is a half-integer. A parallel line of research has focused on the synthesis of high-spin metal-cyanide clusters via bridge-forming reactions between metal complexes with terminal cyanide ligands and metal complexes with suitable leaving groups.<sup>2</sup> Here, the use of precursor species exhibiting orbitally degenerate electronic ground states, such as those associated with octahedral complexes of  $\text{Mn}^{\text{III}}$  or low-spin  $\text{Fe}^{\text{III}}$ , has often provided the magnetic anisotropy needed to create a relaxation barrier.<sup>2a,i-1</sup> With  $2E_g$  ground states, the pentagonal bipyramidal complexes  $[\text{Mo}(\text{CN})_7]^{4-}$  and  $[\text{Re}(\text{CN})_7]^{3-}$  represent simple, high-anisotropy building units that have not yet been incorporated into molecular clusters.<sup>3</sup> Significantly,  $[\text{Mo}(\text{CN})_7]^{4-}$  was found to react with  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  to form extended framework solids displaying strongly anisotropic bulk magnetism.<sup>4</sup> In addition, the results of electronic structure calculations suggest that molecules containing  $[\text{Mo}(\text{CN})_7]^{4-}$  with attached  $\text{Mn}^{\text{II}}$  centers should have high relaxation barriers.<sup>5</sup> Herein, we show that reaction of  $[\text{Re}(\text{CN})_7]^{3-}$  with a capped  $\text{Mn}^{\text{II}}$  complex generates a pentanuclear cluster exhibiting the largest relaxation barrier yet observed for a cyano-bridged single-molecule magnet.

The pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine ( $\text{PY5Me}_2$ )<sup>6,7</sup> was selected as a capping moiety suitable for ensuring the formation of discrete, star-like clusters that are magnetically well-isolated. Reaction of  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_7]$  with 4 equiv of  $[(\text{PY5Me}_2)\text{Mn}(\text{MeCN})](\text{PF}_6)_2$  in acetonitrile produced an immediate blue solution that changed color to green and then yellow in the course of less than 1 min. Given the previously recognized tendency for  $[\text{Re}(\text{CN})_7]^{3-}$  to undergo a one-electron reduction upon cyanide bridge formation,<sup>3b</sup> it was hypothesized that this color change was associated with the spontaneous, solvent-assisted reduction of  $\text{Re}^{\text{IV}}$  ( $S = 1/2$ ) to  $\text{Re}^{\text{III}}$  ( $S = 0$ ) within the cluster product. Indeed, performing the reaction at  $-40^\circ\text{C}$  resulted in the blue, temperature-sensitive solid  $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_5 \cdot 6\text{H}_2\text{O}$  (**1**), whereas workup of the yellow product obtained at room temperature afforded  $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_4 \cdot 10\text{H}_2\text{O}$  (**2**). Additionally, a cyclic voltammogram of a solution of **2** in acetonitrile at  $-35^\circ\text{C}$  was found to exhibit a quasireversible couple at  $E_{1/2} = 0.010\text{ V}$  versus  $[\text{FeCp}_2]^{0/1+}$  (see Figure S1 in the Supporting Information).

Diffusion of diethylether vapor into the yellow reaction solution produced yellow, parallelepiped-shaped crystals of  $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot 4\text{MeCN} \cdot \text{Et}_2\text{O}$  (**2'**). X-ray analysis revealed the  $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$  cluster depicted in Figure 1, with a structure consisting of a central  $[\text{Re}(\text{CN})_7]^{4-}$  complex connected through cyanide bridges to four surrounding  $[(\text{PY5Me}_2)\text{Mn}]^{2+}$  units. The coordination geometry of the  $\text{Re}^{\text{III}}$  center is close to that of an ideal pentagonal bipyramid, with equatorial  $\text{C}_{\text{eq}}-\text{Re}-\text{C}_{\text{eq}}$  bond angles in the range  $71.4(4)^\circ$ – $73.3(2)^\circ$ , near the ideal value of  $72^\circ$ , and an essentially linear axial  $\text{C}_{\text{ax}}-\text{Re}-\text{C}_{\text{ax}}$  angle of  $179.8(5)^\circ$ . While the  $\text{Re}-\text{C}\equiv\text{N}$  angles of  $174.8(8)$ – $179.5(9)^\circ$  are close to linear,

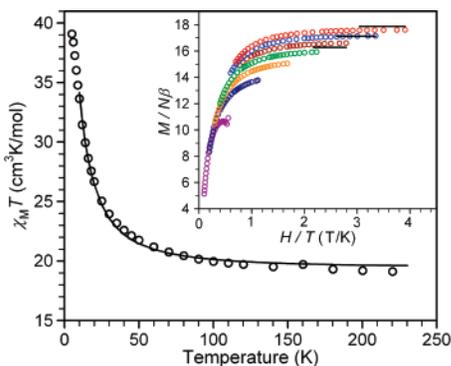


**Figure 1.** Crystal structure of the  $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$  cluster, as observed in **2'**. Red, orange, gray, and blue spheres represent Re, Mn, C, and N, respectively. Selected mean interatomic distances ( $\text{\AA}$ ) and angles (deg) from the structures of **1'** and **2'**, respectively:  $\text{Re}-\text{C}$  2.07(3), 2.07(3);  $\text{Mn}-\text{N}_{\text{CN}}$  2.18(3), 2.11(9);  $\text{Mn}-\text{N}_{\text{py}}$  2.22(8), 2.25(8);  $\text{Re}\cdots\text{Mn}$  5.28(4), 5.21(5);  $\text{Re}-\text{C}\equiv\text{N}$  176.4(3), 178(1),  $\text{Mn}-\text{N}\equiv\text{C}$  154(1), 154(3);  $\text{C}_{\text{eq}}-\text{Re}-\text{C}_{\text{eq}}$  72.1(8), 72.2(8);  $\text{C}_{\text{ax}}-\text{Re}-\text{C}_{\text{ax}}$  90.0(8), 90.0(2);  $\text{C}_{\text{ax}}-\text{Re}-\text{C}_{\text{ax}}$  178(1), 178(1).

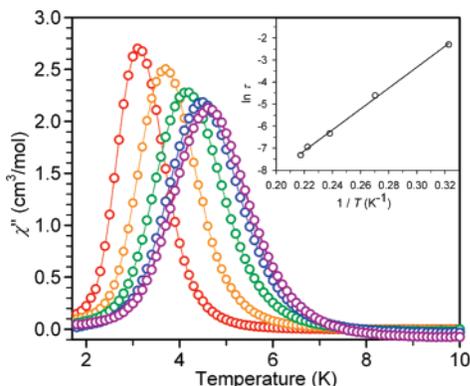
the  $\text{Mn}-\text{N}\equiv\text{C}$  angles of  $149(1)^\circ$ – $164.9(8)^\circ$  deviate significantly from linearity. Such bent angles are not uncommon for  $\text{Mn}^{\text{II}}$  centers coordinated at the nitrogen end of cyanide<sup>2e</sup> and, in this case, may arise from steric conflicts between  $\text{PY5Me}_2$  groups. Overall, the arrangement of the four  $\text{Mn}^{\text{II}}$  centers can be described as a slightly distorted square, with two of the metals binding axial cyanide ligands and the other two binding non-neighboring equatorial cyanide ligands. Similar star-like cluster geometries have been produced using central hexa-<sup>2f</sup> and octacyanometalate<sup>8</sup> complexes but never previously with a heptacyanometalate complex.

Diffusion of diethylether vapor into the chilled blue reaction solution produced blue, parallelepiped-shaped crystals of  $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_5 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$  (**1'**). X-ray analysis revealed the same cluster connectivity present in **2'**, with no substantial distortions of the geometry (see legend of Figure 1). Although severe disorder among the  $\text{PF}_6^-$  anions and guest solvent molecules prevented crystallographic confirmation of the charge state of the cluster, the results of elemental analyses and mass spectrometry experiments support the assignment of a  $5+$  charge (see Supporting Information). In the latter case, electrospray ionization spectra acquired for blue acetonitrile solutions of **1** using a quadrupole time-of-flight mass spectrometer revealed a set of peaks with an isotope distribution clearly corresponding to that of  $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_3\}^{2+}$ . Importantly, this set of peaks was never observed in analogous measurements performed on yellow acetonitrile solutions of **2**.

Dc magnetic susceptibility data collected for **1** are also consistent with the presence of an  $S = 1/2$   $[\text{Re}(\text{CN})_7]^{3-}$  complex, which results in magnetic exchange interactions with the four surrounding  $S =$



**Figure 2.** Variable-temperature dc magnetic susceptibility data for **1** collected in an applied field of 1000 Oe. Inset: Low-temperature magnetization data for **1** collected in applied fields of 1 (purple), 2 (dark blue), 3 (orange), 4 (green), 5 (maroon), 6 (blue), and 7 (red) T. The solid lines represent fits to the data.



**Figure 3.** Out-of-phase ac magnetic susceptibility data for **1**, collected at switching frequencies of 1 (red), 10 (orange), 500 (green), 1030 (blue), and 1488 (purple) Hz. Inset: An Arrhenius plot affording  $U_{\text{eff}} = 33 \text{ cm}^{-1}$ .

$5/2 \text{ Mn}^{\text{II}}$  centers (see Figure 2). With decreasing temperature,  $\chi_M T$  rises monotonically, indicating the presence of ferromagnetic exchange coupling. Below 50 K,  $\chi_M T$  climbs rapidly, reaching a value of  $39 \text{ cm}^3\text{K/mol}$  at 5 K but remaining below the value  $60 \text{ cm}^3\text{K/mol}$  expected for an  $S = 21/2$  ground state in the absence of zero-field splitting. Assuming an exchange Hamiltonian of the form  $\hat{H} = -2J\hat{S}_{\text{Re}} \cdot (\hat{S}_{\text{Mn}(1)} + \hat{S}_{\text{Mn}(2)} + \hat{S}_{\text{Mn}(3)} + \hat{S}_{\text{Mn}(4)})$ , the data above 10 K were fit using MAGFIT 3.<sup>19</sup> to give  $J = 2.3 \text{ cm}^{-1}$  and  $g = 2.00$ . Although  $J$  values for cyano-bridged clusters incorporating high-spin  $\text{Mn}^{\text{II}}$  centers are typically small,<sup>26</sup> an explanation for the exchange coupling being ferromagnetic rather than antiferromagnetic is not immediately forthcoming.<sup>10</sup>

Variable-field magnetization data collected at low temperatures are consistent with the cluster in **1** having a high-spin ground state with significant zero-field splitting (see inset in Figure 2). The weak exchange coupling within the cluster gives rise to low-lying spin excited states, such that only the lowest temperature (below ca. 2.3 K) and highest field (above ca. 4 T) data reflect the true spin ground state. By employing these data and ANISOFIT 2.0,<sup>2d</sup> the most reasonable fit was obtained for  $S = 21/2$  with  $D = -0.44 \text{ cm}^{-1}$ ,  $E = 0.01 \text{ cm}^{-1}$ , and  $g = 2.00$ . This result suggests that  $[(\text{PY5Me}_2)_4\text{-Mn}_4\text{Re}(\text{CN})_7]^{5+}$  should be a single-molecule magnet with a relaxation barrier of  $U = (S^2 - 1/4)|D| = 48 \text{ cm}^{-1}$ .

The frequency dependence of the out-of-phase component of the ac magnetic susceptibility data measured for **1** confirms single-molecule magnet behavior (see Figure 3). Assuming the observed maxima in  $\chi''_M$  correspond to matches between the magnetization relaxation rate ( $\tau^{-1}$ ) and the switching frequency of the ac field, the data should follow the Arrhenius expression  $\ln \tau = U_{\text{eff}}/k_B T +$

$\ln \tau_0$ . Indeed, a plot of  $\ln \tau$  versus  $1/T$  is linear, with a least-squares fit giving  $\tau_0 = 2.4 \times 10^{-8} \text{ s}$  and an effective relaxation barrier of  $U_{\text{eff}} = 33 \text{ cm}^{-1}$ . Significantly, although it is still below the record barrier of  $60 \text{ cm}^{-1}$  for a metal-oxo cluster,<sup>1d</sup> this represents a substantial increase over the previous record of  $22 \text{ cm}^{-1}$  for a cyano-bridged cluster.<sup>21</sup>

In distinct contrast to **1**, magnetic susceptibility data for **2** reveal the simple paramagnetism expected for a molecule containing four high-spin  $\text{Mn}^{\text{II}}$  centers in the absence of exchange coupling (see Figure S5). Thus, loss of spin at the Re center upon reduction switches off the single-molecule magnet behavior of  $[(\text{PY5Me}_2)_4\text{-Mn}_4\text{Re}(\text{CN})_7]^{5+}$ . Future experiments will attempt to probe this unprecedented one-electron switching capability in single-molecule transistors incorporating the cluster.<sup>11</sup>

**Acknowledgment.** This research was funded by NSF Grant No. CHE-0617063. We thank Dr. B. M. Bartlett for assistance and the Miller Foundation for providing D.M.J. with a postdoctoral fellowship.

**Supporting Information Available:** Complete experimental details (PDF). X-ray crystallographic files (CIF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Foltig, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (c) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: New York, 2006 and references therein. (d) Milios, C. J.; Vinslava, A.; Wernsdorfer, W.; Moggach, S.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2007**, *129*, 2754.
- (2) (a) Sculler, A.; Mallah, T.; Verdager, M.; Nivorozhkin, A.; Tholence, J. L.; Veillet, P. *New J. Chem.* **1996**, *20*, 1. (b) Van Langenberg, K.; Batten, S. R.; Berry, K. J.; Hockless, D. C. R.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **1997**, *36*, 5006. (c) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (d) Shores, M. P.; Sokol, J. J.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2279. (e) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656. (f) Marvaud, V.; Decroix, C.; Sculler, A.; Tuyères, F.; Guyard-Duhayon, C.; Vaissermann, J.; Marrot, J.; Gonnet, F.; Verdager, M. *Chem.—Eur. J.* **2003**, *9*, 1692. (g) Berlinguette, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523. (h) Beltran, L. M. C.; Long, J. R. *Acc. Chem. Res.* **2005**, *38*, 325. (i) Li, D. F.; Parkin, S.; Wang, G. B.; Yee, G. T.; Prosvirin, A. V.; Holmes, S. M. *Inorg. Chem.* **2005**, *44*, 4903. (j) Wang, C.-F.; Zuo, J.-L.; Bartlett, B. M.; Song, Y.; Long, J. R.; You, X.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 7162. (k) Glaser, T.; Heidemeier, M.; Weyhermüller, T.; Hoffmann, R.-D.; Rupp, H.; Müller, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 6033. (l) Yoon, J. H.; Lim, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2006**, *45*, 9613.
- (3) (a) Hursthouse, M. B.; Malik, K. M. A.; Soares, A. M.; Gibson, J. F.; Griffith, W. P. *Inorg. Chim. Acta* **1980**, *45*, L81. (b) Bennett, M. V.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 2394.
- (4) (a) Larionova, J.; Clérac, R.; Sanchiz, J.; Kahn, O.; Golhen, S.; Ouahab, L. *J. Am. Chem. Soc.* **1998**, *120*, 13088. (b) Larionova, J.; Kahn, O.; Golhen, S.; Ouahab, L.; Clérac, R. *J. Am. Chem. Soc.* **1999**, *121*, 3349.
- (5) Mironov, V. S.; Chibotaru, L. F.; Ceulemans, A. *J. Am. Chem. Soc.* **2003**, *125*, 9750.
- (6) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, *10*, 2205.
- (7) The closely related ligand 2,6-bis(bis(2-pyridyl)methoxymethane)pyridine (PY5) has been more widely utilized but can be difficult to prepare in large quantities. See: Grebbink, R. J. M. K.; Jonas, R. T.; Stack, T. D. P. *Inorg. Chem.* **2002**, *41*, 4633.
- (8) Herrera, J. M.; Marvaud, V.; Verdager, M.; Marrot, J.; Kalisz, M.; Mathonière, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5468.
- (9) Schmitt, E. A. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1995.
- (10) We note, however, that while the exchange interactions within the extended solid  $\text{K}_2[\text{Mn}(\text{H}_2\text{O})_2][\text{Mo}(\text{CN})_2]_2 \cdot 6\text{H}_2\text{O}$  were initially assigned as ferromagnetic on the basis of temperature-dependent magnetic data,<sup>4b</sup> they were later seen to be antiferromagnetic by polarized neutron diffraction: Gillon, B.; Goujon, A.; Willemin, S.; Larionova, J.; Desplanches, C.; Ruiz, E.; André, G.; Stride, J. A.; Guérin, C. *Inorg. Chem.* **2007**, *46*, 1090.
- (11) (a) Liang, W.; Shores, M. P.; Bockrath, M.; Long, J. R.; Park, H. *Nature* **2002**, *417*, 725. (b) Jo, M.-H.; Grose, J. E.; Liang, W.; Baheti, K.; Deshmukh, M. M.; Sokol, J. J.; Rumberger, E. M.; Hendrickson, D. N.; Long, J. R.; Park, H.; Ralph, D. C. *Nano Lett.* **2006**, *6*, 2014.

JA077527X