Inorg. Chem. **2004**, *43*, 1606–1608

Raising the Spin-Reversal Barrier in Cyano-Bridged Single-Molecule Magnets: Linear $Mn^{III}_2M^{III}(CN)_6$ (M = Cr, Fe) Species Incorporating $[(5\text{-Brsalen})Mn]^+$ Units

Hye Jin Choi, Jennifer J. Sokol, and Jeffrey R. Long*

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

Received November 17, 2003

Reactions between $K_3[M(CN)_6]$ and $[Mn(5\text{-Brsalen})(H_2O)_2]^+$ (5-Brsalen = *N*,*N*′-ethylenebis(5-bromosalicylidene)aminato dianion) in a mixture of methanol and water afford the compounds $K[(5\text{-Brsalen})_2(H_2O)_2Mn_2M(CN)_6]\cdot 2H_2O$, with M = Cr (**1**) or Fe (**2**). The two compounds are isostructural, each containing a molecular cluster with a linear Mn^{III}–NC–M^{III}–CN–Mn^{III} core and tetragonally elongated coordination about the Mn^{III} centers. Magnetic data indicate the presence of weak exchange interactions within the clusters, giving rise to ground states of $S = {}^5/_2$ and ${}^9/_2$ with significant zero-field splitting. Despite the proximity of spin-excited states, ac susceptibility data reveal frequency-dependent out-of-phase signals characteristic of single-molecule magnets with spin-reversal barriers of $U_{eff} = 16$ and 25 cm^{-1}, respectively.

Over a decade ago, it was discovered that the negative axial zero-field splitting parameter *D* associated with the *S* = 10 ground state of $[Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4]$ gives rise to slow paramagnetic relaxation.[1] The ensuing search for molecules with a larger spin-reversal barrier ($U = S^2|D|$ or $(S^2 - {}^1/_4)|D|$ for integer and half-integer values of *S*, respectively) has since yielded a range of transition metal−oxo species exhibiting similar behavior.[2] The highest barrier observed for such a single-molecule magnet, however, is still just $U_{eff} = 56$ cm^{-1}, occurring in the bromoacetate-substituted analogue of the original $Mn_{12}O_{12}$ cluster.[3] Recently, many researchers have focused upon synthesizing metal−cyanide clusters, for which the parameters *S* and *D* are more readily varied within a structure type via substitution of different transition metal ions.[4,5] Thus, for example, replacing the Cr^{III} centers in $[(Me_3tacn)_6MnCr_6(CN)_{18}]^{2+}$ with Mo^{III} was shown to increase anisotropy, generating a barrier of $U_{eff} = 10$ cm^{-1}.[5c,e] Surprisingly, few of the cyano-bridged molecules tested for this behavior have included Mn^{III} ions,[4h,5f] which provide the main source of anisotropy in the $Mn_{12}O_{12}$ clusters. Herein, we report that linear $Mn_2M(CN)_6$ (M = Cr, Fe) species incorporating Schiff base Mn^{III} complexes indeed behave as single-molecule magnets.

A tetragonal elongation in the octahedral coordination geometry of a high-spin Mn^{III} complex has long been known to result in a $^5B_{1g}$ ground state with negative axial zero-field splitting.[6] For Schiff base complexes in particular, the magnitude of the distortion is comparable to that observed in $[Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4]$,[7] and *D* values tend to fall within the range −1 to −4 cm^{-1}.[8] Such complexes have been shown to react with hexacyanometalate ions to produce a variety of cyano-bridged frameworks[9] and molecular clusters.[5f,9ac,10] Among the latter species, $[(5\text{-Brsalen})_2(H_2O)_2Mn_2Fe(CN)_6]^-$ caught our attention, owing to its proposed geometry in which the elongation axes for the two Mn^{III} centers are collinear.[9a] Moreover, the magnetic susceptibility

* Author to whom correspondence should be addressed. E-mail: jlong@cchem.berkeley.edu.

(1) (a) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, J. B.; Folting, 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.

(2) Selected references: (a) Barra, A.-L.; Debrunner, P.; Gatteschi, D.; Schulz, C. E.; Sessoli, R. *Europhys. Lett.* **1996**, *35*, 133. (b) Aubin, S. M. J.; Wemple, M. W.; Adams, D. M.; Tsai, H.-L.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 7746. (c) Castro, S. L.; Sun, Z.; Grant, C. M.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1998**, *120*, 2365. (d) Barra, A. L.; Caneschi, A.; Cornia, A.; Fabrizi de Biani, F.; Gatteschi, D.; Sangregorio, C.; Sessoli, R.; Sorace, L. *J. Am. Chem. Soc.* **1999**, *121*, 5302. (e) Brechin, E. K.; Soler, M.; Davidson, J.; Hendrickson, D. N.; Parsons, S.; Christou, G. *Chem. Commun.* **2002**, 2252. (f) Murrie, M.; Teat, S. J.; Stoeckli-Evans, H.; Güdel, H. U. *Angew. Chem., Int. Ed.* **2003**, *42*, 4653.

(3) Tsai, H.-L.; Chen, D.-M.; Yang, C.-I.; Jwo, T.-Y.; Wur, C.-S.; Lee, G.-H.; Wang, Y. *Inorg. Chem. Commun.* **2001**, *4*, 511.

(4) Selected references: (a) Mallah, T.; Auberger, C.; Verdaguer, M.; Veillet, P. *J. Chem. Soc., Chem. Commun.* **1995**, 61. (b) Scuiller, A.; Mallah, T.; Verdaguer, M.; Nivorzkhin, A.; Tholence, J.-L.; Veillet, P. *New J. Chem.* **1996**, *20*, 1. (c) Oshio, H.; Tamada, O.; Onodera, H.; Ito, T.; Ikoma, T.; Tero-Kubota, S. *Inorg. Chem.* **1999**, *38*, 5686. (d) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoashi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (e) Larionova, J.; Gross, M.; Andres, H.; Stoeckli-Evans, H.; Gudel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605. (f) Parker, R. J.; Spiccia, L.; Berry, K. J.; Fallon, G. D.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2001**, 333. (g) Lescouezec, R.; Vaisserman, J.; Lloret, F.; Julve, M. Verdaguer, M. *Inorg. Chem.* **2002**, *41*, 5943. (h) Berlingeutte, C. P.; Vaughn, D.; Cañada-Vilata, C.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523. (i) Marvaud, V.; Decroix, C.; Scuiller, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, F.; Verdaguer, M. *Chem. Eur. J.* **2003**, *9*, 1678.

(5) (a) Heinrich, J. L.; Berseth, P. A.; Long, J. R. *Chem. Commun.* **1998**, 1231. (b) Berseth, P. A.; Sokol, J. J.; Shores, M. P.; Heinrich, J. L.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 9655. (c) Heinrich, J. L.; Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Solid State Chem.* **2001**, *159*, 293. (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) Choi, H. J.; Sokol, J. J.; Long, J. R. *J. Phys. Chem. Solids*, in press.

(6) Gerritsen, H. J.; Sabisky, E. S. *Phys. Rev.* **1963**, *132*, 1507.

(7) Lis, T. *Acta Crystallogr. B* **1980**, *36*, 2042.

(8) Kennedy, B. J.; Murray, K. S. *Inorg. Chem.* **1985**, *24*, 1552.

10.1021/ic035327q CCC: $27.50
Published on Web 02/10/2004

data for this cluster were interpreted as indicating the presence of ferromagnetic exchange coupling and a negative axial zero-field splitting,[9a] making it a good candidate for a single-molecule magnet.

The cluster-containing compounds $K[(5\text{-Brsalen})_2(H_2O)_2\text{-}Mn_2M(CN)_6]\cdot 2H_2O$, where M = Cr (**1**) and Fe (**2**), were synthesized by direct combination of their molecular components. A solution of $K_3[Cr(CN)_6]$ (41 mg, 0.13 mmol) in 1 mL of water was added to a solution of $[Mn(5\text{-Brsalen})\text{-}(H_2O)_2]ClO_4$ (69 mg, 0.11 mmol) in 10 mL of methanol, and the mixture was stirred for 30 min to give a yellow-brown precipitate. The solid was collected by filtration, washed with 6 mL of a 1:1 mixture of methanol and water, and dried in air to give 51 mg (70%) of **1**.[11] An analogous procedure yielded 230 mg (73%) of **2**, also as a yellow-brown solid.[12] In each case, dark brown plate-shaped crystals suitable for X-ray analysis[13] were obtained simply by layering the solutions of the reactants.

Compounds **1** and **2** are isostructural, both containing a linear $[(5\text{-Brsalen})_2(H_2O)_2Mn_2M(CN)_6]^-$ cluster in which an octahedral $[M(CN)_6]^{3-}$ complex is sandwiched between a pair of $[Mn(5\text{-Brsalen})(H_2O)]^+$ units. As shown for **1** in Figure 1, the Mn^{III} centers are bound through the nitrogen ends of trans cyanide groups, with a long Mn−N(1) separation of 2.342(4) Å and a significantly bent Mn−N(1)−C(1) angle of 141.8(4)°. The opposing coordination site on each Mn^{III} center is taken up by a water molecule, with a Mn−O(3) separation of 2.220(4) Å. As expected, these distances are significantly longer than those associated with the 5-Brsalen ligand, which binds with mean Mn−N and Mn−O distances of 1.985(2) and 1.886(2) Å, respectively. The resulting ratio of axial:equatorial ligand distances is 1.18, only slightly higher than the corresponding ratio of 1.13 in the structure of $[Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4]\cdot 2CH_3CO_2H\cdot 4H_2O$.[7] Although not perfectly collinear, the elongation axes associated with the two Mn^{III} centers in the cyano-bridged cluster are rigorously parallel by virtue of its crystallographic inversion symmetry. Note that the bromine substituents on the 5-Brsalen ligand appear to be essential for forming such trinuclear species, since related reactions employing the less sterically demanding salen ligand instead lead to the heptanuclear clusters $[(salen)_6(H_2O)_6Mn_6M(CN)_6]^{3+}$.[10] While these larger molecules can have a higher-spin ground state, they do not necessarily exhibit the negative axial zero-field splitting parameter required of a single-molecule magnet, perhaps as a consequence of the conflicting orientations of the elongation axes about the Mn^{III} centers.[5f]

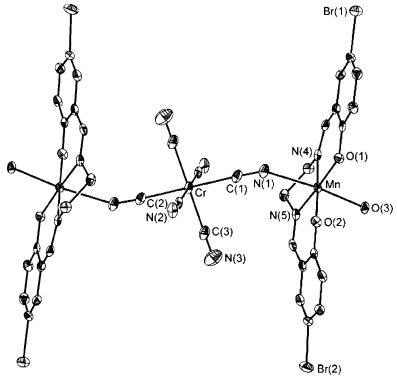

Figure 1. Structure of the linear $[(5\text{-Brsalen})_2(H_2O)_2Mn_2Cr(CN)_6]^-$ cluster in **1**; H atoms are omitted for clarity. The molecule resides on an inversion center within the crystal. Selected interatomic distances (Å) and angles (deg): mean Cr−C 2.071(2), mean C≡N 1.155(3), Mn−N(4) 1.981(3), Mn−N(5) 1.988(3), Mn−O(1) 1.873(3), Mn−O(2) 1.898(3), Mn−N(1) 2.342(4), Mn−O(3) 2.220(4), C(1)−Cr−C(2) 89.9(2), C(2)−Cr−C(3) 92.9-(2), C(1)−Cr−C(3) 89.5(2), Cr−C(1)−N(1) 176.9(4), Cr−C(2)−N(2) 176.6(4), Cr−C(3)−N(3) 176.6(4), N(1)−Mn−N(4) 88.8(1), N(1)−Mn−N(5) 85.2(1), N(4)−Mn−O(3) 90.2(1), N(5)−Mn−O(3) 86.4(1), O(1)−Mn−N(1) 94.7(1), O(2)−Mn−N(1) 91.5(1), O(1)−Mn−O(3) 93.7(1), O(2)−Mn−O(3) 88.7(1), N(1)−Mn−O(3) 171.6(1), Mn−C(1)−N(1) 141.8(4).

Dc magnetic susceptibility measurements were performed on **1** to probe the nature of the magnetic exchange coupling within the Mn_2Cr cluster. At 295 K, the compound exhibits $\chi_M T = 6.480$ cm^{3}K/mol, which is somewhat below the spin-only value of 7.878 cm^3 K/mol expected for one Cr^{III} ($S = {}^3/_2$) and two Mn^{III} ($S = 2$) centers with $g = 2.00$ and in the absence of any exchange coupling. With decreasing temperature, $\chi_M T$ drops steadily to 3.924 cm^3 K/mol at 40 K, and then more precipitously to 1.255 cm^{3}K/mol at 5 K (see Figure S1 in the Supporting Information). The initial trend indicates the presence of antiferromagnetic exchange coupling between the Cr^{III} and Mn^{III} centers, affording an $S = {}^5/_2$ ground state. Indeed, the data above 40 K were readily fit using MAGFIT 3.1[14] and an exchange Hamiltonian of the form $\hat{H} = -2J\hat{S}_{Cr}\cdot(\hat{S}_{Mn(1)} + \hat{S}_{Mn(2)})$ to give $J = -6.3$ cm^{-1} and $g = 1.912$. This represents significantly stronger coupling than apparent in $[(salen)_6(H_2O)_6Mn_6Cr(CN)_6]^{3+}$, for which $J = -2.5$ cm^{-1}.[5f] A similar trend wherein J diminishes as the number of exchange pathways increases has been noted previously for cyano-bridged clusters.[5d] In accord with the field dependence of the magnetization data for **1** (see Figure S2, Supporting Information), the enhanced decay of $\chi_M T$ at very low temperatures is attributed to zero-field splitting in the $S = {}^5/_2$ ground state of the Mn_2Cr cluster.

As shown in the upper panel of Figure 2, compound **2** exhibits substantially different magnetic behavior. At 295

(9) (a) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981. (b) Miyasaka, H.; Matsumoto, N.; Re, N.; Gallo, E.; Floriani, C. *Inorg. Chem.* **1997**, *36*, 670. (c) Miyasaka, H.; Ieda, H.; Matsumoto, N.; Re, N.; Crescenzi, R.; Floriani, C. *Inorg. Chem.* **1998**, *37*, 255. (d) Miyasaka, H.; Ieda, H.; Matsumoto, N.; Sugiura, K.-I.; Yamashita, M. *Inorg. Chem.* **2003**, *42*, 3509.

(10) (a) Shen, X.; Li, B.; Zou, J.; Xu, Z. *Transition Met. Chem.* **2002**, *27*, 372. (b) Shen, X.; Li, B.; Zou, J.; Hu, H.; Xu, Z. *J. Mol. Struct.* **2003**, *657*, 325.

(11) Characterization of **1**. IR (solid, ATR): ν_{CN} 2140, 2122 cm^{-1}. $\mu_{eff} = 7.16\ \mu_B$ at 295 K. Anal. Calcd for $C_{38}H_{32}Br_4CrKMn_2N_{10}O_8$: C, 35.72; H, 2.53; N, 10.97. Found: C, 35.98; H, 2.52; N, 10.86. The X-ray powder diffraction pattern for this compound matches that simulated from its crystal structure.[13]

(12) Characterization of **2**. IR (solid, ATR): ν_{CN} 2128, 2109 (sh), 2100 cm^{-1}. $\mu_{eff} = 6.95\ \mu_B$ at 295 K. Anal. Calcd for $C_{38}H_{32}Br_4\text{-}FeKMn_2N_{10}O_8$: C, 35.62; H, 2.52; N, 10.93. Found: C, 35.47; H, 2.46; N, 10.93. The X-ray powder diffraction pattern for this compound matches that simulated from its crystal structure.[13]

(13) Crystal and structure refinement parameters: **1**, $C_{38}H_{32}Br_4CrKMn_2N_{10}O_8$, $T = 154$ K, $P2_1/c$, $Z = 2$, $a = 10.820(3)$ Å, $b = 14.054(4)$ Å, $c = 15.320(4)$ Å, $V = 2320.3(10)$ Å^3, $d_{calc} = 1.828$ g/cm^3, $R_1 = 0.0502$, $wR_2 = 0.0998$; **2**, $C_{38}H_{32}Br_4FeKMn_2N_{10}O_8$, $T = 154$ K, $P2_1/c$, $Z = 2$, $a = 10.8285(18)$ Å, $b = 13.972(2)$ Å, $c = 15.154(3)$ Å, $V = 2282.7\text{-}(7)$ Å^3, $d_{calc} = 1.852$ g/cm^3, $R_1 = 0.0529$, $wR_2 = 0.0994$. Data were collected using graphite monochromated Mo Kα radiation, and corrected for Lorentz, polarization, and absorption effects. The structures were refined against all data using SHELXTL 5.0.

(14) Schmitt, E. A. Ph.D. Thesis, University of Illinois, 1995.

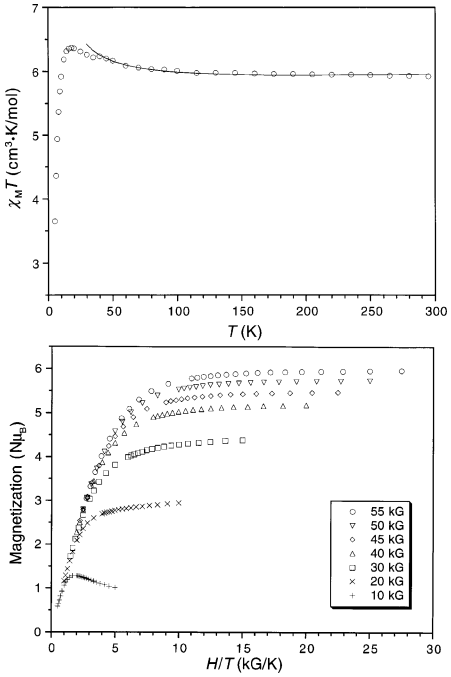

Figure 2. Magnetic behavior of **2**. Upper: Dc molar susceptibility data, as measured in an applied field of 10 kG. The solid line represents a calculated fit to the data; see text for details. Lower: Magnetization data in applied fields from 10 to 55 kG at temperatures between 2 and 20 K.

K, $\chi_M T$ is 5.927 cm^3 K/mol, only slightly less than the spin-only value of 6.378 cm^3 K/mol expected for one Fe^{III} ($S = {}^1/_2$) ion and two Mn^{III} ($S = 2$) ions with $g = 2.00$ and in the absence of any exchange coupling. With decreasing temperature, $\chi_M T$ gradually increases, achieving a maximum of 6.372 cm^3 K/mol at 18 K before plummeting. The rise in $\chi_M T$ indicates ferromagnetic coupling between the Fe^{III} and Mn^{III} centers, resulting in an $S = {}^9/_2$ ground state. Employing the same procedure as before, the data above 30 K were fit to give $J = 2.3$ cm^{-1} and $g = 1.900$.[15] The coupling constant is in close agreement with the value of $2J = 4.5$ cm^{-1} obtained for this compound previously by a different fitting method.[9a] The drop in $\chi_M T$ at very low temperatures is again attributable to zero-field splitting.

Of the two clusters, $[(5\text{-Brsalen})_2(H_2O)_2Mn_2Fe(CN)_6]^-$ has the higher spin ground state, and was therefore studied most intensively. The lower panel in Figure 2 shows the field dependence of the magnetization data for compound **2** at temperatures between 2 and 20 K. The nonsuperposition of the isofield lines clearly indicates the presence of significant zero-field splitting. Additionally, even at 55 kG and 2 K, the magnetization is still well below the saturation value of 8.55 Nμ_B expected for an $S = {}^9/_2$ ground state with $g = 1.900$ in the absence of zero-field splitting. Efforts to extract reliable zero-field splitting parameters from these data, however, were severely hampered by the presence of low-lying spin-excited states. Specifically, the very weak ferromagnetic exchange coupling within the cluster leads to $S = {}^7/_2$ and $S = {}^5/_2$ states located 2.3 and 4.6 cm^{-1} above the ground state, respectively. As a consequence, zero-field splittings on the order of 1 cm^{-1} in magnitude associated with any or all of these states results in mixing of the corresponding M_S levels. While reasonable simulations of the data could be obtained using three independent D values for these three lowest-energy spin states, the results are probably not reliable owing to overparametrization.

(15) Note that this fit did not take the orbital degeneracy of the Fe^{III} center into account, and is therefore only approximate.

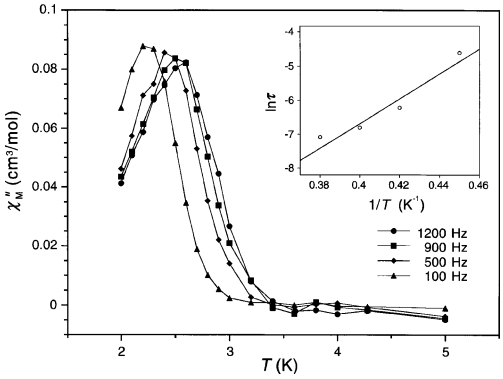

Figure 3. Out-of-phase component of the ac susceptibility for **2**, measured in a 1 G field oscillating at selected frequencies. The plot in the inset shows that the relaxation times, τ, obtained from the peaks in the ac susceptibility conform to an Arrhenius relationship.

Despite the proximity of lower-spin excited states, ac magnetic susceptibility data collected on **2** in zero applied dc field manifest slow relaxation of the magnetization. As the frequency of the oscillating 1 G field increases, a lag in the in-phase component of the molar ac susceptibility, χ_M', is observed at low temperatures (see Figure S3, Supporting Information). The corresponding rise in the out-of-phase susceptibility, χ_M'' is shown in Figure 3 for switching frequencies of 100, 500, 900, and 1200 Hz. In each case, χ_M'' achieves a maximum at a temperature where it is assumed that the switching of the magnetic field matches the relaxation rate, ${}^1/_\tau$, for the magnetization of the cluster. As for other single-molecule magnets,[1,2] the ensuing relaxation times follow an Arrhenius relationship: $\tau = \tau_0 \exp(U_{eff}/k_B T)$. Accordingly, a plot of ln τ vs $1/T$ is linear (see inset in Figure 3), with a least-squares fit yielding $\tau_0 = 5.5 \times 10^{-10}$ s and $U_{eff} = 25$ cm^{-1}. Assuming that the slow relaxation stems exclusively from the $S = {}^9/_2$ ground state, the 25 cm^{-1} barrier sets a limit on the associated zero-field splitting parameter of $D \leq -1.3$ cm^{-1}, which is very close to the value reported previously.[9a]

Interestingly, although the Mn_2Cr cluster possesses a ground state of just $S = {}^5/_2$, it too behaves as a single-molecule magnet. A completely analogous interpretation of the ac susceptibility data for **1** (see Figures S4 and S5, Supporting Information) gave $\tau_0 = 6.1 \times 10^{-8}$ s and $U_{eff} = 16$ cm^{-1}.

The foregoing results demonstrate the highest spin-reversal barriers yet observed for cyano-bridged single-molecule magnets. Efforts to incorporate Schiff base complexes of Mn^{III} into longer chain clusters with higher-spin ground states are underway.

Acknowledgment. This research was funded by NSF Grant CHE-0072691 and the Korean Science & Engineering Foundation (through a postdoctoral fellowship to H.J.C.). We thank Profs. J. K. McCusker and A. M. Stacy for use of the SQUID magnetometers.

Supporting Information Available: X-ray crystallographic files (CIF) and additional magnetic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035327Q