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A Cyano-Bridged Single-Molecule Magnet: Slow Magnetic Relaxation in a Trigonal Prismatic $MnMo_6(CN)_{18}$ Cluster

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Received April 1, 2002

Select transition metal clusters have been found to exhibit magnetic bistability at low temperature.[1] Such species, dubbed single-molecule magnets, possess a high-spin ground state (S), which, when combined with a negative axial zero-field splitting ($D < 0$), leads to an energy barrier for spin reversal. To date, all of the molecules firmly established as displaying this behavior incorporate oxo-based bridging ligands that mediate the magnetic exchange coupling between metal centers. However, in the interest of producing clusters with larger spin reversal barriers, much attention has focused on developing cyano-bridged cluster systems, for which the parameters S and D are more readily adjusted via substitution of various metal ions.[2−4] Recently, it was demonstrated that replacing Cr^{III} with Mo^{III} in the linear cluster $[(Me_3tacn)_2(cyclam)NiCr_2(CN)_6]^{2+}$ (Me_3tacn = N,N',N''-trimethyl-1,4,7-triazacyclononane; cyclam = 1,4,8,11-tetraazacyclotetradecane) prompts a substantial increase in the magnitude of D associated with the $S = 4$ ground state.[3d] Herein, we show that an analogous substitution in the trigonal prismatic cluster $[(Me_3tacn)_6MnCr_6(CN)_{18}]^{2+}$,[3c] bearing a higher spin ground state of $S = {}^{13}/_2$, generates the first well-documented example of a cyano-bridged single-molecule magnet.

The $MnMo_6$ cluster was synthesized by an assembly reaction paralleling the one known to afford its chromium-containing analogue.[3c] A tan solution of $KClO_4$ (15 mg, 0.11 mmol), $Mn(ClO_4)_2\cdot6H_2O$ (45 mg, 0.12 mmol), and $[(Me_3tacn)Mo(CN)_3]$[3d] (60 mg, 0.17 mmol) in 15 mL of water was concentrated to a volume of 10 mL under a flow of dinitrogen. A small quantity of colorless solid was removed by filtration, and the filtrate was further concentrated to a volume of 0.5 mL. The ensuing green-brown block-shaped crystals were collected by filtration, washed with successive aliquots of water (10 mL) and methanol (20 mL), and dried in air to give 43 mg (60%) of $K[(Me_3tacn)_6MnMo_6(CN)_{18}](ClO_4)_3$ (**1**).[5]

X-ray analysis of a crystal of **1** revealed the compound to be isostructural with $K[(Me_3tacn)_6MnCr_6(CN)_{18}](ClO_4)_3$.[3c,6] Figure 1 displays the structure of the $[(Me_3tacn)_6MnMo_6(CN)_{18}]^{2+}$ cluster, in which six $[(Me_3tacn)Mo(CN)_3]$ units surround a central Mn^{II} ion. The coordination of this Mn^{II} ion by the nitrogen ends of six cyanide ligands approximates a trigonal prismatic geometry, with rigorously parallel triangular faces twisted about the 3-fold axis 22.6° away from the fully eclipsed position. As in the chromium-containing structure, the deviation of its coordination environment from the more usual octahedral geometry is attributed to interactions between peripheral cyanide ligands and the K^+ cations in the crystal lattice.[3c,7] A comparison of the interatomic distances and angles in the structures of the chromium- and molybdenum-containing clusters reveals only minor differences, all of which are commensurate with the larger radius of the Mo^{III} ion.

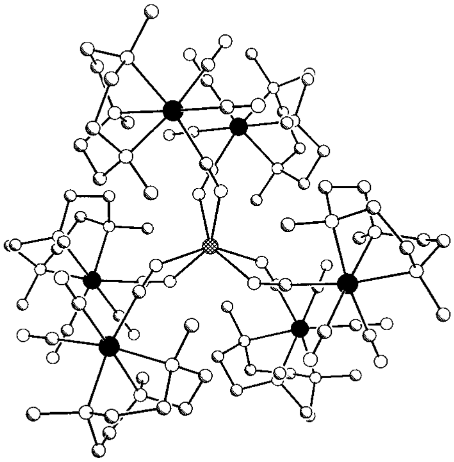

Figure 1. Structure of the trigonal prismatic $[(Me_3tacn)_6MnMo_6(CN)_{18}]^{2+}$ cluster in **1**. Crosshatched, black, shaded, and white spheres represent Mn, Mo, C, and N atoms, respectively; H atoms are omitted for clarity. The cluster exhibits crystallographically imposed D_3 symmetry, with the Mn atom positioned on the 3-fold rotation axis. Selected mean interatomic distances (Å) and angles (deg): Mo−C 2.13(1), Mn−N 2.278, C−N 1.161(7), Mo−N 2.236(8), C−Mo−C 91(1), Mo−C−N 178(2), N−Mn−N 80.5, 84.8, Mn−N−C 149.2, C−Mo−N 95(1), N−Mo−N 80.0(3).

DC magnetic susceptibility measurements were performed on **1** to probe the nature of the magnetic exchange coupling within the $MnMo_6$ cluster. The variation of χ_MT with temperature is plotted in the inset in the upper panel of Figure 2. At 295 K, its value is 11.8 cm^3K/mol, somewhat below the spin-only value of 15.625 cm^3K/mol expected for one Mn^{II} ($S = {}^5/_2$) ion and six Mo^{III} ($S = {}^3/_2$) ions in the absence of any exchange coupling. With decreasing temperature, χ_MT drops, reaching a minimum at approximately 115 K before rising steeply to a maximum of 21.4 cm^3K/mol at 12 K. This behavior is consistent with weak antiferromagnetic coupling between the Mn^{II} and Mo^{III} ions, giving rise to an $S = {}^{13}/_2$ ground state. The data above 12 K were fit with MAGFIT 3.1[8] and an exchange Hamiltonian of the form $\hat{H} = -2J[\hat{S}_{Mn}\cdot(\hat{S}_{Mo(1)} + \hat{S}_{Mo(2)} + \hat{S}_{Mo(3)} + \hat{S}_{Mo(4)} + \hat{S}_{Mo(5)} + \hat{S}_{Mo(6)})]$, resulting in a coupling constant of $J = -6.7$ cm^{-1} and $g = 1.90$. This represents an increase in magnitude over the coupling of $J = -3.0$ cm^{-1} observed for the analogous $MnCr_6$ cluster.[3c] Such an enhancement in the strength of the exchange coupling has been observed previously in comparing the ferromagnetically coupled clusters $[(Me_3tacn)_2(cyclam)NiM_2(CN)_6]^{2+}$ (M = Cr, Mo),[3b,d] and presumably originates from the more diffuse d orbitals of Mo^{III}.

The downturn in χ_MT below 12 K is primarily due to the presence of zero-field splitting, the effects of which are also discernible in the magnetization data shown at the top of Figure 2. Assuming an $S = {}^{13}/_2$ ground state and negligible population of excited spin states, the magnetization data for $T \leq 6$ K were fit with ANISOFIT[3d] to give zero-field splitting parameters of $D = -0.33$ cm^{-1} and $E =$

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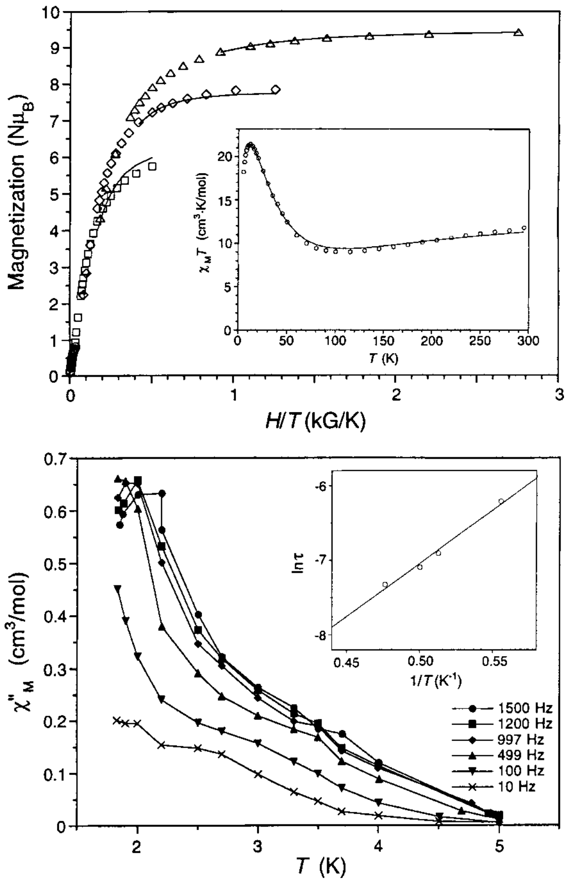

Figure 2. Magnetic behavior of **1**. Upper: DC magnetization and susceptibility data, as measured in applied fields of 1 (circles), 10 (squares), 25 (diamonds), and 55 (triangles) kG. Solid lines represent calculated fits to the data; see text for details. Lower: Out-of-phase component of the AC susceptibility in a 1 G field oscillating at a variety of 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.

-0.018 cm^{-1} with $g = 1.57$.[9] The significant increase in the magnitude of D relative to that of the original MnCr$_6$ cluster stems from the greater spin−orbit coupling associated with the Mo^{III} ion. If the sign and magnitude of D obtained from the fit are correct, then the MnMo$_6$ cluster should be a single-molecule magnet with a spin reversal barrier of $U = (S^2 - {}^1/_4)\cdot|D| = 14$ cm^{-1}.

AC magnetic susceptibility data collected in the zero applied DC field confirm that the cluster indeed behaves as a single-molecule magnet. 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 S1 in the Supporting Information). The corresponding rise in the out-of-phase susceptibility, χ_M'', is depicted in Figure 2 (lower). For the highest frequencies measured, 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. In accord with other single-molecule magnets,[1] the ensuing relaxation times follow an Arrhenius relationship: $\tau = \tau_0 \exp(U/k_BT)$. A plot of $\ln\tau$ vs $1/T$ is linear (see inset in the lower panel of Figure 2), with a least-squares fit indicating $\tau_0 = 7 \times 10^{-7}$ s and $U = 10$ cm^{-1}. Thus, the apparent spin reversal energy barrier is in reasonable agreement with our previous estimate of 14 cm^{-1}, but is still significantly less than the record barrier of 50 cm^{-1} observed for [Mn$_{12}$O$_{12}$(CH$_3$CO$_2$)$_{16}$(H$_2$O)$_4$].[1a,b,10]

It is hoped that substitutions of the type exemplified here can be applied to even higher spin metal−cyanide clusters, generating single-molecule magnets with much larger spin reversal barriers. Ultimately, such molecules may find applications in information storage or spin-based molecular electronics devices.

Acknowledgment. This research was supported by NSF Grant No. CHE-0072691, the Camille and Henry Dreyfus Foundation, and the Alfred P. Sloan Foundation. We thank Dr. C. Crawford and Unilever for a donation of Me$_3$tacn, Profs. J. K. McCusker and A. M. Stacy for use of the SQUID magnetometers, and Prof. D. N. Hendrickson for supplying software used to fit the magnetic susceptibility data.

Supporting Information Available: Plots of the temperature dependence of χ_M' for **1** and tables of crystallographic information for the structure of **1** (PDF), as well as 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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(5) Characterization of **1**: IR (solid, ATR) υ_{CH} 2982, 2925, 2882, 2833, υ_{CN} 2111, 2094 cm^{-1}. $\mu_{eff} = 9.71$ μ_B at 295 K. Anal. Calcd for C$_{72}$H$_{126}$Cl$_3$KMnMo$_6$N$_{36}$O$_{12}$: C, 35.10; H, 5.15; N, 20.46. Found: C, 34.88; H, 5.26; N, 20.35.

(6) Crystal and structure refinement parameters for **1**: C$_{72}$H$_{126}$Cl$_3$KMnMo$_6$N$_{36}$O$_{12}$, $T = 154$ K, $P\bar{3}1c$, $Z = 2$, $a = 14.2312(4)$ Å, $c = 28.143(1)$ Å, $V = 4936.2(3)$ Å^3, $d_{calc} = 1.658$ g/cm^3, $R_1 = 0.0514$, $wR_2 = 0.1280$. Data were collected on a Siemens SMART diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, and were corrected for Lorentz, polarization, and absorption effects. The structure was refined against all data with SHELXTL 5.0.

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JA0263846