Select transition metal clusters have been found to exhibit magnetic bistability at low temperature. Such species, dubbed single-molecule magnets, possess a high-spin ground state, 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. Recently, it was demonstrated that replacing CrIII with MoVI in the linear cluster [(Me3tacn)2-(cyclam)NiCr6(CN)18]2+ (Me-tacn = N,N,N′,N″-trimethyl-1,4,7-triazaazacyclotetradecane; cyclam = 1,4,8,11-tetraazacyclotetradecane) prompts a substantial increase in the magnitude of the magnet.

Figure 1. Structure of the trigonal prismatic [(Me3tacn)6MnMo6(CN)18]2- cluster. 1 Crosshatched, black, shaded, and white spheres represent Mn, Cr, and Mo, respectively; H atoms are omitted for clarity. The cluster exhibits crystallographically imposed D3 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 1.161-1.7, Mo-N 2.236(8), C-Mo-C 91(1), Mn-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 MnMo6 cluster. The variation of χM(T) with temperature is plotted in the inset in the upper panel of Figure 2. At 295 K, its value is 11.8 cm3 K/mol, somewhat below the spin-only value of 15.625 cm3 K/mol expected for one MnII (S = 3/2) ion and six MoVI (S = 7/2) ions in the absence of any exchange coupling. With decreasing temperature, χM(T) drops, reaching a minimum at approximately 115 K before rising steeply to a maximum of 21.4 cm3 K/mol at 12 K. This behavior is consistent with weak antiferromagnetic coupling between the MnII and MoVI ions, giving rise to an S = 13/2 ground state. The data above 12 K were fit with MAGFIT 3.1 and an exchange Hamiltonian of the form $H = -2\left[\hat{S}_{\text{Mn}} \cdot \hat{S}_{\text{Mo}} \cdot (\hat{S}_{\text{Mo}} + \hat{S}_{\text{Mn}}\right] + \hat{S}_{\text{Mo}} \cdot \hat{S}_{\text{Mn}}$, resulting in a coupling constant of $J = -6.7 \text{ cm}^{-1}$. This represents an increase in magnitude over the coupling of $J = -3.0 \text{ cm}^{-1}$ observed for the analogous MnCr6 cluster. Such an enhancement in the strength of the exchange coupling has been observed previously in comparing the ferromagnetically coupled clusters [(Me3tacn)(cyclam)-NiM2(CN)18]2+ (M = Cr, Mo)2,4 and presumably originates from the more diffuse d orbitals of MoVI.

The downturn in χM(T) 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 ≤ 6 K were fit with ANISOFIT24 to give zero-field splitting parameters of D = -0.33 cm-1 and E =

---

A Cyano-Bridged Single-Molecule Magnet: Slow Magnetic Relaxation in a Trigonal Prismatic MnMo6(CN)18 Cluster

Jennifer J. Sokol, Allan G. Hee, and Jeffrey R. Long*

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

Received April 1, 2002
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 Me₃taen, Prof. 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 χM 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.

References


(5) Characterization of 1: IR (solid, ATR) νCN 2925, 2925, 2882, 2833, νC=C 1111, 2044 cm⁻¹, νMo= 971 μm⁻¹ at 295 K. Anal. Caled for Cu₃H₆Cl₂K₂MoN₆O₃: 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: C₁₂H₁₅ClK₂Mn₆N₆O₃, T = 154 K, P31c, Z = 2, a = 14.2321(4) Å, c = 29.1431(1) Å, V = 4936.2(3) Å³, dcal = 1.658 g/cm³, R₁ = 0.0514, wR₂ = 0.1280. Data were collected on a Siemens SMART four-circle diffractometer with graphite monochromated Mo Kα radiation, and were corrected for Lorentz, polarization, and absorption effects. The structure was refined against all data with SHELXTL 5.0.


(9) It is not yet clear why the g factor for the ground state should be so low, and efforts to substantiate this result with high-frequency high-field EPR spectroscopy are underway. The magnetization data shown in Figure 2 were verified with an independent measurement employing a different SQUID magnetometer.