

**A Trigonal-Bipyramidal Cyanide Cluster with Single-Molecule-Magnet Behavior: Synthesis, Structure, and Magnetic Properties of $[\text{Mn}^{\text{II}}(\text{tmphen})_2]_3[\text{Mn}^{\text{III}}(\text{CN})_6]_2$ ****

Curtis P. Berlinguette, Derek Vaughn, Cristina Cañada-Vilalta, José Ramón Galán-Mascarós, and Kim R. Dunbar*

Molecules that exhibit magnetic bistability, commonly referred to as single-molecule magnets (SMMs), are of high interest because of their unusual physical properties and potential applications in quantum computing.^[1] In contrast to traditional magnets, which are characterized by the bulk ordering of spins within a 3D solid, SMM behavior arises from the intrinsic magnetic properties of the individual molecules. The signature of an SMM is a slow paramagnetic relaxation of the magnetization evidenced by a frequency-dependent out-of-phase (χ''_m) ac susceptibility signal and hysteretic behavior. The presence of an appreciable thermal barrier for reversing the magnetization is related to the combination of a large total spin ground state (S) and negative uniaxial anisotropy (D). The existence of the phenomenon of single-molecule magnetism was first noted a decade ago in the compound $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{OH}_2)_4]$, which displays a ground state of $S=10$.^[2] Since this discovery, a number of oxo-bridged clusters containing V,^[3] Mn,^[4–6] Fe,^[7] Co,^[8] and Ni^[9] have also been shown to display SMM behavior. In all cases, the molecules that have longer paramagnetic relaxation times have values of $S > 3$ or higher and a negative D value.

In considering the prospects for preparing non-oxide SMMs, we turned our attention to chemistry inspired by the face-centered Prussian-blue solids. The recognition that bimetallic Prussian-blue solids exhibit spontaneous magnetization at temperatures as high as 376 K^[10] prompted an extrapolation of this chemistry to the realm of magnetic

[*] Prof. K. R. Dunbar, C. P. Berlinguette, D. Vaughn
Department of Chemistry, Texas A&M University
PO Box 30012, College Station, TX 77842-3012 (USA)
Fax: (+1) 979-845-7177
E-mail: dunbar@mail.chem.tamu.edu

C. Cañada-Vilalta
Department of Chemistry, Indiana University
Bloomington, IN 47405 (USA)

Dr. J. R. Galán-Mascarós
Instituto de Ciencia Molecular, Universidad de Valencia
Dr. Moliner, 50, 46100 Burjassot (Spain)

[**] The authors thank Prof. Ernest R. Davidson for the program used for the reduced magnetization fitting. K.R.D. gratefully acknowledges the National Science Foundation for a Nanoscale Science and Engineering (NIRT) Grant (DMR-0103455), the Telecommunication&Informatics Task Force (TITF 2001-3), and for equipment grants to purchase the CCD X-ray equipment (CHE-9807975) and the SQUID magnetometer (NSF-9974899).



Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

molecules. This goal can be accomplished by introducing capping ligands to circumvent the formation of the face-centered cubic structure. Among the metal cyanide clusters prepared by this general strategy are molecular squares, cubes, and other more complex architectures.^[11] Despite the large ground-state spin values detected for several molecules (e.g., $S = 27/2$, $39/2$, $51/2$),^[12] SMM behavior has not been confirmed in any of these cases, a fact that is generally attributed to the lack of sufficient single-ion and/or shape anisotropy. A recent report of a trigonal-prismatic cluster, however, has provided evidence that magnetic bistability can indeed exist in a cyanide-bridged molecule.^[13]

One of the goals of our research program in cyanide chemistry is to introduce magnetically anisotropic metal ions into clusters, the symmetry of which allows the existence of an easy axis of magnetization. Herein we describe the first results of these efforts, namely the synthesis, X-ray structure analysis, and magnetic behavior of $[[\text{Mn}^{\text{II}}(\text{tmphen})_2]_3[\text{Mn}^{\text{III}}(\text{CN})_6]_2]$ (**1**; tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) whose unique axis of symmetry is a C_3 axis on which the Mn^{III} ions reside.

Slow diffusion of solutions of $[\text{K}([18]\text{crown-6})]_3\text{-}[\text{Mn}(\text{CN})_6]$ and $\text{Mn}^{\text{II}}(\text{tmphen})_2(\text{NO}_3)_2$ in acetonitrile led to the formation of X-ray quality yellow needles of compound **1**.^[14] The molecular geometry of **1** is that of a trigonal bipyramid in which low-spin Mn^{III} ($S = 1$) ions occupy the apical positions and high-spin Mn^{II} ($S = 5/2$) ions reside in the equatorial plane (Figure 1).^[15] Each Mn^{III} ion is linked by three nearly linear cyanide bridges to Mn^{II} centers and is capped by three terminal cyanide ligands. The Mn^{II} ions are coordinated to *cis*-tmphen ligands as well as to the N ends of two cyanide bridges. The Mn^{II} centers in each molecule have a homochiral coordination geometry, but the crystal is racemic, as evidenced by the fact that the compound crystallizes in a centrosymmetric space group ($P2_1/c$). The presence of the

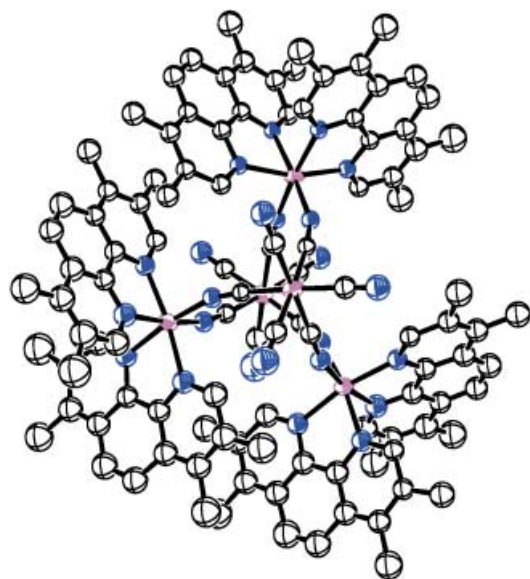


Figure 1. Molecular structure of **1** (thermal ellipsoids set at the 50% probability level, H atoms are omitted for clarity); Mn: purple; N: blue.

methylated phenanthroline ligands prevents the clusters from packing with close intermolecular metal distances (the closest intermolecular $\text{Mn}\cdots\text{Mn}$ distance is 8.77 Å).

Magnetic susceptibility measurements were performed on crushed single crystals of **1** at 1000 G in the temperature range 1.8–300 K (Figure 2). The room temperature $\chi_m T$ value of $\sim 13.70 \text{ emu K mol}^{-1}$ is slightly lower than the expected spin-only value of $15.125 \text{ emu K mol}^{-1}$, which can be attributed to a value of $g < 2$. The $\chi_m T$ value decreases as the temperature is lowered to $10.41 \text{ emu K mol}^{-1}$ at 45 K, after which point $\chi_m T$ increases to a maximum of $15.69 \text{ emu K mol}^{-1}$ at 4.0 K. The magnetic behavior below 45 K is indicative of a strong antiferromagnetic interaction between the paramagnetic centers, which stabilizes a high-spin ground state. The least-squares fit of the reduced magnetization data (Figure 3) indicates an $S = 11/2$ ground state with $g = 1.784(2)$ and $D = -0.348(3) \text{ cm}^{-1}$.^[16] The calculated D parameter supports the conclusion that compound **1** is an SMM with a thermal barrier for magnetization reversal of $U = (S^2 - 1/4) |D| = 10 \text{ cm}^{-1}$.

One of the characteristics of an SMM is the observation of an out-of-phase (χ_m'') ac susceptibility signal. To probe the dynamics of the magnetization relaxation of compound **1**, ac susceptibility measurements were performed in a 3 G ac field

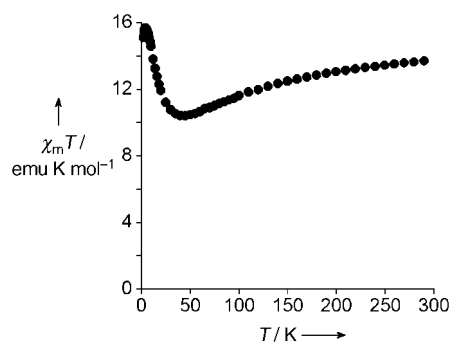


Figure 2. Temperature dependence of $\chi_m T$ versus T for a crushed crystalline sample of **1** in a 1000 G applied DC field.

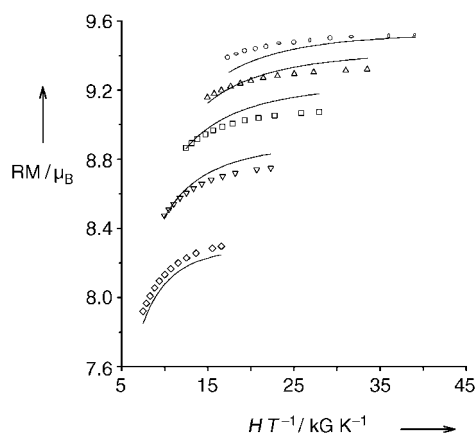


Figure 3. Reduced magnetization (RM) versus the ratio of the external field and temperature (HT^{-1}) for **1**. The solid lines are the best fit of the data to an $S = 11/2$ ground state with $g = 1.784(2)$ and $D = -0.348 \text{ cm}^{-1}$. Data were measured at 30 (\diamond), 40 (∇), 50 (\square), 60 (\triangle), and 70 kG (\circ).

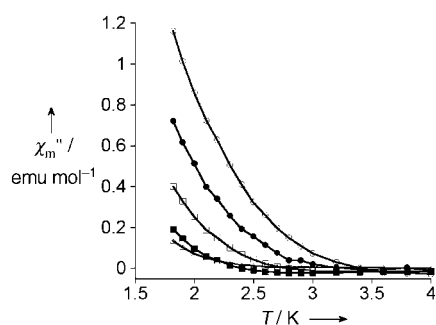


Figure 4. Frequency dependence of the out-of-phase (χ''_m) ac magnetic susceptibility versus T for **1**. Data were measured at 1 (Δ), 6 (\blacksquare), 32 (\square), 178 (\bullet), and 1000 Hz (\circ).

oscillating at 1–1500 Hz in the temperature range of 1.8–8.0 K (Figure 4) on the same sample of crystals that was used for the dc studies. The in-phase magnetic susceptibility signal (χ'_m) follows the expected behavior for a paramagnetic system. In addition to the χ'_m signal, the compound exhibits an out-of-phase (χ''_m) signal below 4 K (Figure 4). Although no maximum was observed down to 1.8 K, there is an obvious frequency dependence of the χ''_m signal consistent with SMM behavior. Noteworthy, the magnitude of the χ''_m signal relative to the χ'_m signal is comparable to that of the Mn_{12} SMM family, a good sign that the χ''_m response is not an artifact. Lower temperature measurements (<1.8 K) are in progress to confirm whether the frequency dependence is in accord with Arrhenius behavior, and to check for hysteresis.

The title compound is important to the field of SMMs, as it is a rare example of a cyanide-based molecule that exhibits this behavior. The role of the anisotropic Mn^{III} ions in the trigonal-bipyramidal (tbp) molecular geometry appears to be crucial for dictating this magnetic phenomenon. Previous studies have demonstrated that isostructural clusters of the type $\{[\text{Fe}(\text{CN})_6]_2[\text{Ni}(\text{N}(\text{N})_2)_3]\}$ do not exhibit SMM behavior.^[15] This observation lends further credence to the idea that incorporating anisotropic ions into these clusters is fundamentally important for observing slow relaxation, and must be considered along with S in the design of new SMMs. Plans are in progress to investigate systematically the role of the metal ion in the two different positions of the tbp cluster (apical versus equatorial) in determining the sign and magnitude of the D parameter of these clusters. The main targets are anisotropic metal ions such as Co^{II} and Re^{III} . Armed with comprehensive magnetic data for a homologous series of paramagnetic clusters, we hope to gain more insight into how different parameters affect the ability of a molecule to act as a single-molecule magnet.

Experimental Section

A solution of $[\text{Mn}(\text{tmphen})_2(\text{NO}_3)_2]$ was prepared by combining $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (75 mg, 0.3 mmol) with two equivalents of tmphen (140 mg, 0.6 mmol) in acetonitrile (50 mL). A solution of $[\text{K}(\text{[18]crown-6})_3][\text{Mn}(\text{CN})_6]$ was prepared in situ by stirring an excess of $\text{K}_3[\text{Mn}(\text{CN})_6]$ (200 mg, 0.7 mmol) in a solution of [18]crown-6 (240 mg, 0.9 mmol) in acetonitrile (50 mL). The two solutions were slowly combined and the reaction mixture was left to stand undisturbed for one week. Yellow X-ray quality crystals of **1**

were obtained: Yield = 45 mg (~15%). IR (Nujol): $\tilde{\nu}$ = 2138, 2131, 2113, 2068 cm^{-1} ; $\nu(\text{C}\equiv\text{N})$.

Received: November 5, 2002 [Z50479]

Keywords: cluster compounds · cyanides · magnetic properties · manganese · single-molecule studies

- [1] a) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, 25, 66–71; b) D. D. Awschalom, D. P. DiVincenzo, *Phys. Today* **1995**, 48, 43–48.
- [2] a) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, 115, 1804–1816; b) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, 365, 141–143.
- [3] S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1998**, 120, 2365–2375.
- [4] a) H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, 117, 301–317; b) S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L.-C. Brunel, A. L. Rheingold, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **1999**, 38, 5329–5340.
- [5] a) W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, G. Christou, *Nature* **2002**, 416, 406–409; b) S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1996**, 118, 7746–7754.
- [6] a) C. Boskovic, W. Wernsdorfer, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **2002**, 41, 5107–5118; b) E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E. C. Sanudo, T. R. Concolino, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **2002**, 124, 9710–9711.
- [7] A. L. Barra, P. DeBrunner, D. Gatteschi, C. E. Schultz, R. Sessoli, *Europhys. Lett.* **1996**, 35, 133–138.
- [8] E. C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, M. Ledezma-Gairaud, G. Christou, *J. Appl. Phys.* **2002**, 91, 7382–7384.
- [9] S. T. Ochsenbein, M. Murrie, E. Rusanov, H. Stoeckli-Evans, C. Sekine, H. U. Güdel, *Inorg. Chem.* **2002**, 41, 5133–5140.
- [10] S. D. Holmes, G. S. Girolami, *J. Am. Chem. Soc.* **1999**, 121, 5593–5594.
- [11] a) J. J. Sokol, M. P. Shores, J. R. Long, *Angew. Chem.* **2001**, 113, 242–245; *Angew. Chem. Int. Ed.* **2001**, 40, 236–239; b) K. K. Klausmeyer, S. R. Wilson, T. B. Rauchfuss, *J. Am. Chem. Soc.* **1999**, 121, 2705–2711; c) J. A. Smith, J. R. Galán-Mascarós, R. Clerac, J. S. Sun, O. Y. Xiang, K. R. Dunbar, *Polyhedron* **2001**, 20, 1727–1734.
- [12] a) A. Scüller, T. Mallah, M. Verdager, A. Nivorozhkin, J. L. Tholence, P. Veillet, *New J. Chem.* **1996**, 20, 1–3; b) Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. Ohkoshi, K. Hashimoto, *J. Am. Chem. Soc.* **2000**, 122, 2952–2953; c) J. Larionova, G. Mathias, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem.* **2000**, 112, 1667–1672; *Angew. Chem. Int. Ed.* **2000**, 39, 1605–1609.
- [13] A frequency-dependent out-of-phase (χ''_m) signal was observed for the $S=13/2$ ground state cluster $[(\text{Me}_3\text{tacn})_6\text{Mn}^{\text{II}}\text{Mo}_6^{\text{III}}(\text{CN})_{18}]^{2+}$ ($\text{Me}_3\text{tacn} = N, N', N''$ -trimethyl-1,4,7-triazacyclonane); J. J. Sokol, A. G. Hee, J. R. Long, *J. Am. Chem. Soc.* **2002**, 124, 7656–7657.
- [14] $1.7\text{H}_2\text{O}$ ($\text{C}_{112}\text{H}_{110}\text{Mn}_5\text{N}_{26}\text{O}_7$), $M_w = 2209$, monoclinic, $P2_1/c$, $a = 19.724(5)$, $b = 25.379(6)$, $c = 24.411(5)$ Å, $\beta = 99.251(6)^\circ$, $V = 12061(5)$ Å³, $Z = 4$, $T = 110(2)$ K, $\rho_{\text{calc}} = 1.222$ g cm⁻³, $\mu = 6.69$ cm⁻¹, $F(000) = 4604$, 69503 measured reflections, 17418 unique reflections, collected on a SMART 1K area detector diffractometer equipped with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). Refinement (G. M. Sheldrick,

SHELXL-97, University of Göttingen, Göttingen (Germany), **1997**) of 1368 parameters for 8974 independent reflections with $I > 4\sigma(I)$ gave $R1 = 0.0883$, $wR2 = 0.2185$. CCDC-196445 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

- [15] This cluster shape has been observed for other combinations of metals of general formula $\{[\text{Fe}(\text{CN})_6]_2[\text{Ni}(\text{NN})_2]_3\}$ ($\text{NN} = 2$ -pyridylimino nitroxide, bis(1-pyrazolyl)methane, 1,10-phenanthroline): a) K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer, *J. Am. Chem. Soc.* **2000**, *122*, 718–719; b) K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Inorg. Chem.* **1997**, *36*, 5006–5015; c) C. P. Berlinguette, J. R. Galán-Mascarós, K. R. Dunbar, *Inorg. Chem.*, in press.
- [16] The least squares fitting of the reduced magnetization curves with a “+ D ” value was optimized to the parameters: $S = 11/2$, $g = 1.83(2)$, $D = 0.68(7) \text{ cm}^{-1}$, $\text{error} = 0.1$. Error contour plots (D versus g) for the reduced magnetization data confirm the minimum arising from the “− D ” value leads to the global minimum ($\text{error} = 0.05$). For details of these fittings see Supporting Information.