Inorg. Chem. **2009**, *48*, 807−809

Inorganic Chemistry

Communication

$\{Mn_6\}_n$ Single-Chain Magnet Bearing Azides and Di-2-pyridylketone-Derived Ligands

Theocharis C. Stamatatos,[†] Khalil A. Abboud,[†] Wolfgang Wernsdorfer,[‡] and George Christou*,[†]

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and Institut Néel, CNRS and Université J. Fourier, BP 166, 38042 Grenoble Cedex 9, France

Received October 27, 2008

The synthesis, structure, and magnetochemical characterization of a new manganese single-chain magnet are reported. The compound is a chain of repeating Mn_6 units bridged by end-on azide groups and exhibits magnetization hysteresis loops.

The preparation of new polynuclear manganese complexes continues to receive a great deal of attention as a route to compounds with interesting metal topologies and which might function as nanoscale magnetic particles or nanowires. The former are single-molecule magnets (SMMs),[1] molecular species that have a significant barrier to magnetization relaxation arising from the combination of a large ground-state spin, *S*, and easy-axis anisotropy (negative zero-field splitting parameter, *D*). The latter are single-chain magnets (SCMs), and they possess a large uniaxial anisotropy, strong intrachain exchange interactions without spin compensation between the high-spin magnetic units, and good isolation of the chains in order to avoid two- (2D) and three-dimensional (3D) ordering;[2] these lead to an upper limit of the relaxation barrier (Δ) given by $(D + 4J)S^2$, where J is the interaction between repeating units of the chain.[2] Both SMMs and SCMs are of great interest because of their unusual physical properties and their potential use in information storage at the molecular level[3] and as qubits in quantum computation.[4]

There are now many SMMs,[5] but the number of SCMs is still relatively small even though the first one was discovered several years ago.[6] Of the currently known examples, the majority are heterospin systems containing at least two different spin carriers bridged by organic radicals,[6,7] oximate,[2,8] or Prussian blue anions and derivatives[9] and obtained by a direct approach using SMMs as building blocks. Homospin SCMs are relatively rare, and all of them have been synthesized from a self-assembly approach using highly anisotropic metal sources, such as Mn^{III},[10] $Fe^{II/III}$,[11] and Co^{II} ions.[12]

We have recently been investigating the use in Mn^{III} cluster chemistry of the azide (N_3^-) group, which in the end-on 1,1-bridging mode gives ferromagnetic interactions for a wide range of M−N−M angles.[13] We have obtained a variety of new SMMs from an amalgamation of azides and alkoxide-based chelates,[14] such as the recently reported Mn_{24} and Mn_{26} dimers of clusters with N_3^- and the diolate of di-2-

---

* To whom correspondence should be addressed. E-mail: christou@chem.ufl.edu.

[†] University of Florida.

[‡] Institut Néel, CNRS and Université J. Fourier.

(1) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66.

(2) For some recent reviews, see: (a) Miyasaka, H.; Clérac, R. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1727. (b) Coulon, C.; Miyasaka, H.; Clérac, R. *Struct. Bonding (Berlin)* **2006**, *122*, 163. (c) Miyasaka, H.; Yamashita, M. *Dalton Trans.* **2007**, 399.

(3) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133.

(4) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789.

(5) For a review, see: Aromi, G.; Brechin, E. K. *Struct. Bonding (Berlin)* **2006**, *122*, 1, and references cited therein.

(6) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, A.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760.

(7) (a) Bernot, K.; Bogani, L.; Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* **2006**, *128*, 7947. (b) Miyasaka, H.; Madanbashi, T.; Sugimoto, K.; Nakazawa, Y.; Wernsdorfer, W.; Sugiura, K.; Yamashita, M.; Coulon, C.; Clérac, R. *Chem.*−*Eur. J.* **2006**, *12*, 7028. (c) Bernot, K.; Luzon, J.; Sessoli, R.; Vindigni, A.; Thion, J.; Richeter, S.; Leclercq, D.; Larionova, J.; van der Lee, A. *J. Am. Chem. Soc.* **2008**, *130*, 1619.

(8) (a) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. *J. Am. Chem. Soc.* **2002**, *124*, 12837. (b) Miyasaka, H.; Nezu, T.; Sugimoto, K.; Sugiura, K.; Yamashita, M.; Clérac, R. *Chem.*−*Eur. J.* **2005**, *11*, 1592.

(9) For a recent review, see : Lescouëzec, R.; Toma, L. M.; Vaissermann, J.; Verdaguer, M.; Delgado, F. S.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Coord. Chem. Rev.* **2005**, *249*, 2691 and references cited therein.

(10) (a) Xu, H.-B.; Wang, B.-W.; Pan, F.; Wang, Z.-M.; Gao, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 7388. (b) Bai, Y.-L.; Tao, J.; Wernsdorfer, W.; Sato, O.; Huang, R.-B.; Zheng, L.-S. *J. Am. Chem. Soc.* **2006**, *128*, 16428. (c) Lecren, L.; Roubeau, O.; Coulon, C.; Li, Y.-G.; Goff, X. F. L.; Wernsdorfer, W.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 17353. (d) Chakov, N. E.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2004**, *43*, 5919. (e) Brockman, J. T.; Stamatatos, Th. C.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2007**, *46*, 9160.

(11) (a) Tanaka, H.; Kajiwara, T.; Kaneko, Y.; Takaishi, S.; Yamashita, M. *Polyhedron* **2007**, *26*, 2105. (b) Przybylak, S. W.; Tuna, F.; Teat, S. J.; Winpenny, R. E. P. *Chem. Commun.* **2008**, 1983.

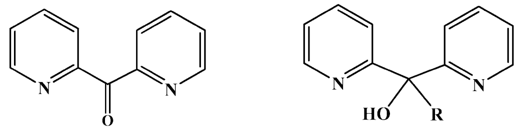
(12) (a) Liu, T.-F.; Fu, D.; Gao, S.; Zhang, Y.-Z.; Sun, H.-L.; Su, G.; Liu, Y.-J. *J. Am. Chem. Soc.* **2003**, *125*, 13976. (b) Zheng, Y.-Z.; Tong, M.-L.; Zhang, W.-X.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6310. (c) Zheng, X.-M.; Hao, Z.-M.; Zhang, W.-X.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3456.

(13) (a) Escuer, A.; Aromi, G. *Eur. J. Inorg. Chem.* **2006**, 4721, and references cited therein. (b) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am.Chem. Soc.* **1998**, *120*, 11122.

(14) For a recent review, see: Stamatatos, Th. C.; Christou, G. *Inorg. Chem.* **2008**, in press.

10.1021/ic8020645 CCC: $40.75

Chart 1. Groups Mentioned in the Text



dpk

dpkdH$_2$ R = OH
dpkmeH$_2$ R = CH$_2$CH(OCH$_3$)(OH)

pyridylketone (dpkd^{2-}; Chart 1).[15] In contrast, the end-to-end 1,3-bridging mode of N_3^- leads to antiferromagnetic coupling[13] but has proven useful for the linking of magnetic units into a variety of one-dimensional (1D), 2D, and 3D networks, and some of the former have been SCMs.[10a,c] In the present work, we report a new SCM composed of repeating Mn$_6$ clusters and which for the first time has end-on azide groups both within the repeating units and as the linkers between them.

The reaction of Mn(ClO$_4$)$_2$·6H$_2$O, dpk, NaO$_2$CMe·3H$_2$O, NaN$_3$, and NEt$_3$ in a 1:1:2:1:1 molar ratio in MeOH/DMF (4:1, v/v) gave a dark-red solution from which was obtained dark-red crystals of [Mn$_6$(N$_3$)$_4$(O$_2$CMe)$_2$(dpkd)$_2$(dpkme)$_2$(MeOH)$_2$]$_n$ (**1**) in 60% yield upon layering with Et$_2$O;[16] dpkme^{2-} is the dianion of a new form of dpkd^{2-} (Chart 1).[17] Compound **1** is a 1D chain containing a mixed-valent Mn$^{II}_4$Mn$^{III}_2$ repeating unit (Figure 1, top) that consists of a central, planar [Mn$^{II}_2$Mn$^{III}_2$] rhombus (Mn1, Mn1′, Mn2, and Mn2′) bridged by two η^1:η^1:μ(end-on)-N_3^- (N5 and N5′) groups and alkoxide (RO$^-$) arms of dpkd^{2-} and dpkme^{2-} groups. The rhombus is additionally linked to two extrinsic Mn^{II} atoms (Mn3 and Mn3′) by RO$^-$ and MeCO$_2^-$ groups. The dpkd^{2-} and dpkme^{2-} groups bind in η^1:η^2:η^3:η^1:μ_4 and η^1:η^2:η^1:η^1:μ modes, respectively; the former is new for dpkd^{2-}, emphasizing the bridging flexibility of this group. Ligation at the extrinsic Mn^{II} atoms is completed by terminal MeOH and N_3^- groups (N8, N8a, N8′, and N8′a), with the latter becoming η^1:η^1:μ (end-on) and bridging the Mn$_6$ unit to its neighbors on either side to give a 1D chain (Figure 1, bottom). The manganese oxidation states were obtained from bond-valence-sum (BVS) calculations[18] and the clear Jahn−Teller (JT) axial elongations (O4′−Mn1−N3) at the near-octahedral Mn^{III} atoms. The Mn^{II} atoms, Mn2 and Mn3, are seven- and six-coordinate with distorted pentagonal-bipyramidal and octahedral geometries, respectively. The shortest Mn···Mn separations between chains are all >10 Å, and there are no significant interchain hydrogen-bonding or π−π-stacking interactions.

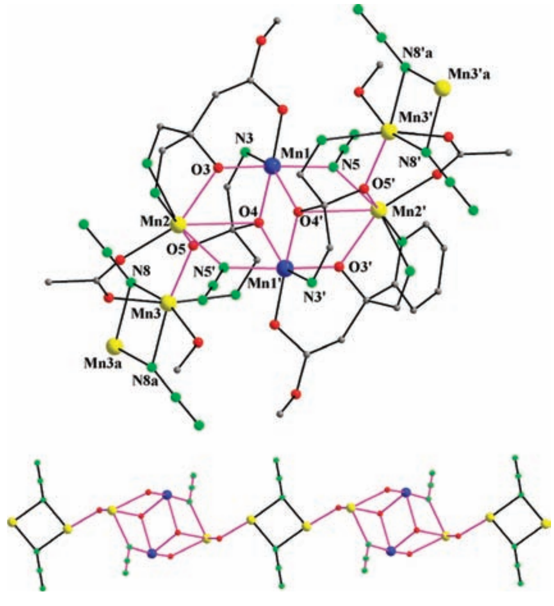


Figure 1. (Top) Labeled PovRay representation of the Mn$_6$ repeating unit of **1**. Only the N and two C atoms of the pyridine rings are shown. H atoms have been omitted for clarity. (Bottom) Section of the 1D chain. Color scheme: Mn^{II}, yellow; Mn^{III}, blue; O, red; N, green; C, gray. Primed, unprimed, a, and a′ atoms are related by symmetry.

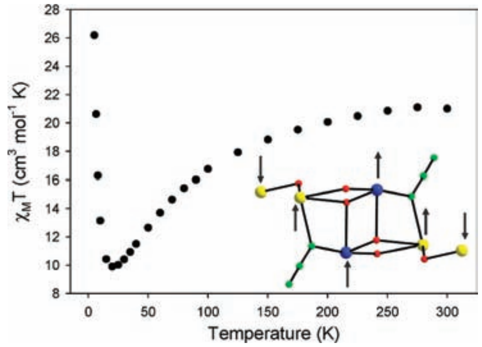


Figure 2. $\chi_M T$ vs T plot for complex **1** in a 1 kG field. Inset: Proposed spin alignments in the repeating Mn$_6$ unit that give its putative $S = 4$ ground state. Color scheme as in Figure 1.

Solid-state direct current (dc) magnetic susceptibility (χ_M) data on dried **1** were collected in a 1 kG (0.1 T) field in the 5.0−300 K range and are plotted as $\chi_M T$ vs T in Figure 2. $\chi_M T$ steadily decreases from 21.00 cm^3 K mol^{-1} at 300 K to a minimum of 9.90 cm^3 K mol^{-1} at 20.0 K and then rapidly increases to 26.19 cm^3 K mol^{-1} at 5.0 K. The shape of the $\chi_M T$ vs T plot indicates some antiferromagnetic intra-Mn$_6$ interactions and ferromagnetic inter-Mn$_6$ interactions, as was expected through the end-on azide groups. The 20.0 K value is suggestive of an $S = 4$ ground state for the Mn$_6$ repeating unit, and this is as expected for a ferromagnetically coupled central rhombus with a resulting $S = 9$ spin and antiferromagnetic coupling between it and the two "extrinsic" Mn^{II} atoms (Figure 2, inset). Note that discrete Mn$^{II}_2$Mn$^{III}_2$ complexes with a [Mn$_4$(μ_3-OR)$_2$(μ-OR)$_4$] core and the same rhombus structure are known to be ferromagnetically coupled with $S = 9$ ground states even without bridging azide groups on two edges as in **1**.[19]

---

(15) Stamatatos, Th. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 6694.

(16) Anal. Calcd (found) for dried **1** (solvent-free): C, 42.12 (42.31); H, 3.66 (3.52); N, 17.54 (17.76). Crystal data for **1**·2MeOH: C$_{56}$H$_{58}$N$_{20}$O$_{16}$Mn$_3$, 1596.84 g mol^{-1}, monoclinic $P2_1/n$, a = 12.104(2) Å, b = 20.330(4) Å, c = 13.557(3) Å, β = 100.317(4)°, Z = 4, V = 3282.0(11) Å^3, d_{calc} = 1.679 g cm^{-3}, T = 173(2) K. Final R1 = 4.67 and wR2 = 11.20%.

(17) For a review in the coordination chemistry of dpk and its unusual derivatives, see: Papaefstathiou, G. S.; Perlepes, S. P. *Comments Inorg. Chem.* **2002**, *23*, 249.

(18) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102. BVS for the Mn^{2+} and Mn^{3+} were 2.05−2.07 and 3.03, respectively.

(19) Yoo, J.; Brechin, E. K.; Yamaguchi, A.; Nakano, M.; Huffman, J. C.; Maniero, A. L.; Brunel, L.-C.; Awaga, K.; Ishimoto, H.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **2000**, *39*, 3615.

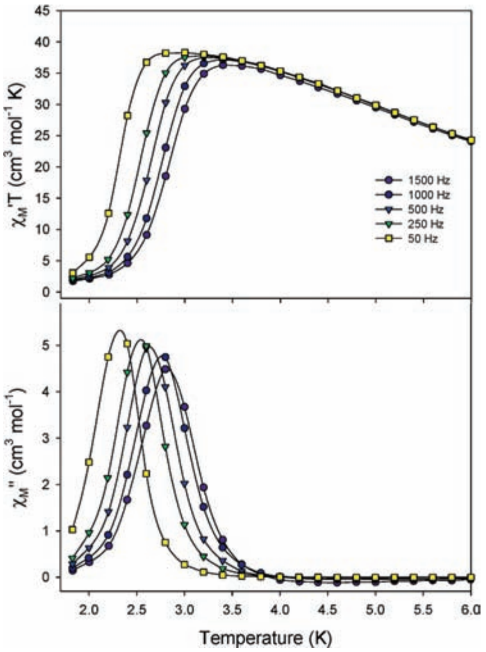


Figure 3. Plot of the in-phase (χ'_M) (as χ'_MT) and out-of-phase (χ''_M) ac susceptibility signals for complex **1**, measured in a 3.5 G field oscillating at the indicated frequencies.

To probe the magnetization dynamics of **1**, alternating current (ac) susceptibility studies were performed in the 1.8−15 K range using a 3.5 G field oscillating at frequencies in the 50−1500 Hz range. The obtained data (Figure 3) reveal that below ~4.0 K both the in-phase (χ_M', as $\chi_M'T$) and out-of-phase (χ_M'') ac susceptibilities are strongly frequency-dependent, and complete χ_M'' peaks are seen above 1.8 K, the operating limit of our magnetometer. These data indicate a significant barrier to magnetization relaxation and preclude 3D ordering.[11b] An Arrhenius plot constructed from the ac χ_M'' vs T data gave $\Delta E = 42$ K and $\tau_0 = 3.5 \times 10^{-11}$ s, where ΔE is the energy barrier for the magnetization relaxation and τ_0 is the preexponential factor.

A scaling procedure[20] applied to the $\chi_M'T$ data of **1** clearly indicates a linear regime characteristic of Ising 1D systems; this is confirmed by the ln($\chi_M'T$) vs 1/T plot,[21] which increases linearly between ~12 and 5 K, giving an energy gap, Δ_ξ, of 8.4 K. It is emphasized that ln($\chi_M'T$) is not decreasing at the lowest temperatures,[21] indicating that the interchain interactions are almost negligible.[20] Moreover, the shift (ΔT_{max}) in the χ_M'' peak maximum temperature (T_{max}) with ac frequency (f) is measured by a parameter $\varphi = (\Delta T_{max}/T_{max})/\Delta(\log f)$, and for **1** we obtained $\varphi = 0.14$, which is in the range of normal superparamagnets[11b,12b] and excludes the possibility of a spin glass.[22] It should be noted that the ΔE barrier extracted from the ac data is significantly larger than Δ_ξ, suggesting that the relaxation mechanism in this SCM cannot be described by a simple Glauber model,[2,23] a situation that is often observed in SCMs consisting of large-cluster repeating units.[10d,e,11b] In such cases, additional contributions associated with the relaxation of the individual cluster units (i.e., Mn_6 in **1**) must be taken into account. We are now exploring the possibility of isolating the Mn_6 repeating unit of **1** in a discrete form to allow a separate study of its magnetization dynamics and a comparison between them and those of **1**. Using data collected at 2.4 K and zero applied dc field, we obtained a near-semicircular Cole−Cole plot (χ_M'' vs χ_M'), which was fitted to a generalized Debye model to give an α parameter of 0.35,[24] indicative of a moderate distribution of relaxation times.[21]

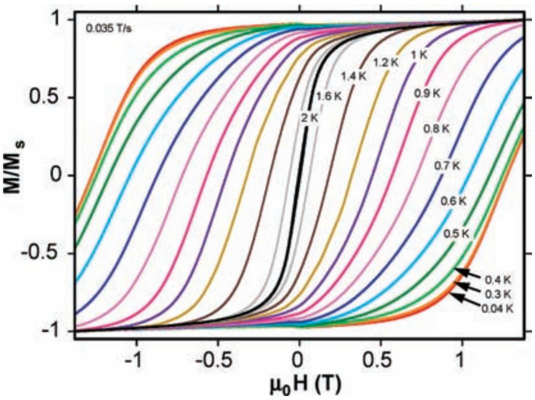


Figure 4. Magnetization (M) vs applied dc field (H) hysteresis loops for a single crystal of **1**·2MeOH at the indicated temperatures. The magnetization is normalized to its saturation value (M_s).

The assignment of compound **1** as an SCM was further confirmed by magnetization vs applied dc field scans on single crystals of **1**·2MeOH using an array of micro-SQUIDs.[25] These scans exhibited magnetization hysteresis loops below 2.0 K, whose coercivities increase with decreasing temperature (Figure 4).[21]

In conclusion, we have shown that the use of dpk-derived chelating/bridging groups and azides in reactions with simple Mn^{II} sources, and in the additional presence of carboxylate ligands, leads to a new SCM comprising Mn_6 repeating units bridged by end-on azide groups. The latter undoubtedly provide ferromagnetic coupling between what we believe are $S = 4$ Mn_6 units. Finally, it should be noted that **1** and the discrete Mn_{26} compound[15] are made by very similar reactions differing only in the identity of the solvent. In addition, their structures are also related, both involving a Mn_x cluster bridged by end-on azide bridges, but differ in that **1** is a chain whereas the Mn_{26} complex is a dumbbell-shaped dimer of clusters. Such results emphasize that there may well be a variety of new SMMs and SCMs waiting to be discovered that involve the linkage by end-on azide bridges of Mn_x clusters into clusters of clusters or 1D chains. Work in this area is continuing.

Acknowledgment. This work was supported by NSF Grant CHE-0414555 (G.C.).

Supporting Information Available: Crystallographic data (CIF format) and magnetism figures for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8020645

---

(20) Coulon, C.; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408.

(21) See the Supporting Information.

(22) $\varphi = 0.01$ is a typical value for a spin glass. For details, see: Mydosh, J. A. *Spin Glasses: An Experimental Introduction*; Taylor & Francis: London, 1993.

(23) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294.

(24) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.

(25) Wernsdorfer, W. *Adv. Chem. Phys.* **2001**, *118*, 99.