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{Mn₆}_n Single-Chain Magnet Bearing Azides and Di-2-pyridylketone-Derived Ligands

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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 groundstate 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 level³ 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

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spin carriers bridged by organic radicals,^{6,7} oximate,^{2,8} or Prussian blue anions and derivatives⁹ 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 (N₃⁻) group, which in the end-on 1,1bridging 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 alkoxidebased chelates,¹⁴ such as the recently reported Mn₂₄ and Mn₂₆ dimers of clusters with N₃⁻ and the diolate of di-2-

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Chart 1. Groups Mentioned in the Text



pyridylketone (dpkd²⁻; Chart 1).¹⁵ In contrast, the end-toend 1,3-bridging mode of N_3^- leads to antiferromagnetic coupling¹³ 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 Mn₆ clusters and which for the first time has endon azide groups both within the repeating units and as the linkers between them.

The reaction of $Mn(ClO_4)_2 \cdot 6H_2O$, dpk, $NaO_2CMe \cdot 3H_2O$, NaN₃, and NEt₃ 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 [Mn₆(N₃)₄(O₂CMe)₂(dpkd)₂(dpkme)₂- $(MeOH)_2]_n$ (1) in 60% yield upon layering with Et₂O;¹⁶ dpkme²⁻ is the dianion of a new form of dpkd²⁻ (Chart 1).¹⁷ Compound 1 is a 1D chain containing a mixed-valent Mn^{II}₄Mn^{III}₂ repeating unit (Figure 1, top) that consists of a central, planar $[Mn^{II}_2Mn^{III}_2]$ rhombus (Mn1, Mn1', Mn2, and Mn2') bridged by two $\eta^1:\eta^1:\mu(\text{end-on})-N_3^-$ (N5 and N5') groups and alkoxide (RO⁻) arms of dpkd²⁻ and dpkme²⁻ groups. The rhombus is additionally linked to two extrinsic Mn^{II} atoms (Mn3 and Mn3') by RO⁻ and MeCO₂⁻ groups. The dpkd²⁻ and dpkme²⁻ groups bind in $\eta^1:\eta^2:\eta^3:\eta^1:\mu_4$ and $\eta^{1}:\eta^{2}:\eta^{1}:\eta^{1}:\mu$ modes, respectively; the former is new for dpkd²⁻, 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



Figure 1. (Top) Labeled PovRay representation of the Mn₆ 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 Mn₆ unit that give its putative *S* = 4 ground state. Color scheme as in Figure 1.

latter becoming $\eta^{1}:\eta^{1}:\mu$ (end-on) and bridging the Mn₆ 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) calculations¹⁸ and the clear Jahn–Teller (JT) axial elongations (O4'–Mn1–N3) at the near-octahedral Mn^{II} atoms. The Mn^{II} atoms, Mn2 and Mn3, are seven- and six-coordinate with distorted pentagonalbipyramidal 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.

Solid-state direct current (dc) magnetic susceptibility $(\chi_{\rm M})$ 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 $\chi_{\rm M}T$ vs T in Figure 2. $\chi_M T$ steadily decreases from 21.00 cm³ K mol^{-1} at 300 K to a minimum of 9.90 cm³ 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-Mn₆ interactions and ferromagnetic inter-Mn₆ interactions, as was expected through the endon azide groups. The 20.0 K value is suggestive of an S = 4 ground state for the Mn₆ 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}₂Mn^{III}₂ complexes with a $[Mn_4(\mu_3-OR)_2(\mu-OR)_4]$ 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

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⁽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 $P_{2_1/n}$, a = 12.104(2) Å, b = 20.330(4) Å, c = 13.557(3) Å, $\beta = 100.317(4)^\circ$, Z = 4, V = 3282.0(11) Å³, $d_{calc} = 1.679$ g cm⁻³, T = 173(2) K. Final R1 = 4.67 and wR2 = 11.20%.



Figure 3. Plot of the in-phase (χ'_{M}) (as $\chi'_{M}T$) 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 outof-phase (χ_M'') ac susceptibilities are strongly frequencydependent, 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 procedure²⁰ 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 largecluster repeating units.^{10d,e,11b} In such cases, additional



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

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

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 Mn₆ 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 Mn₂₆ compound¹⁵ 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_r cluster bridged by endon azide bridges, but differ in that 1 is a chain whereas the Mn₂₆ 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.

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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.

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