

{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 Mn₆ 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 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

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^{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 1,1-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 Mn₂₄ and Mn₂₆ dimers of clusters with N₃⁻ and the diolate of di-2-

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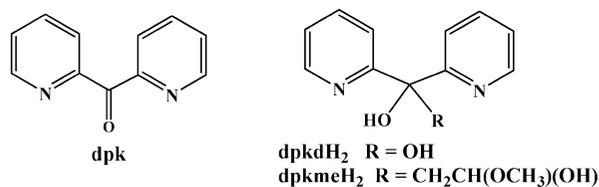
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Chart 1. Groups Mentioned in the Text



pyridylketone (dpkd^{2-} ; Chart 1).¹⁵ In contrast, the end-to-end 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 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 $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, dpk , $\text{NaO}_2\text{CMe} \cdot 3\text{H}_2\text{O}$, 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 $[\text{Mn}_6(\text{N}_3)_4(\text{O}_2\text{CMe})_2(\text{dpk})_2(\text{dpkme})_2(\text{MeOH})_2]_n$ (**1**) in 60% yield upon layering with Et_2O ;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 $\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2$ repeating unit (Figure 1, top) that consists of a central, planar $[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2]$ rhombus (Mn1 , $\text{Mn1}'$, Mn2 , and $\text{Mn2}'$) bridged by two $\eta^1:\eta^1:\mu$ (end-on)- N_3^- (N5 and $\text{N5}'$) 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 $\text{Mn3}'$) by RO^- and MeCO_2^- groups. The dpkd^{2-} and dpkme^{2-} 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 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 , $\text{N8}'$, and $\text{N8}'\text{a}$), with the

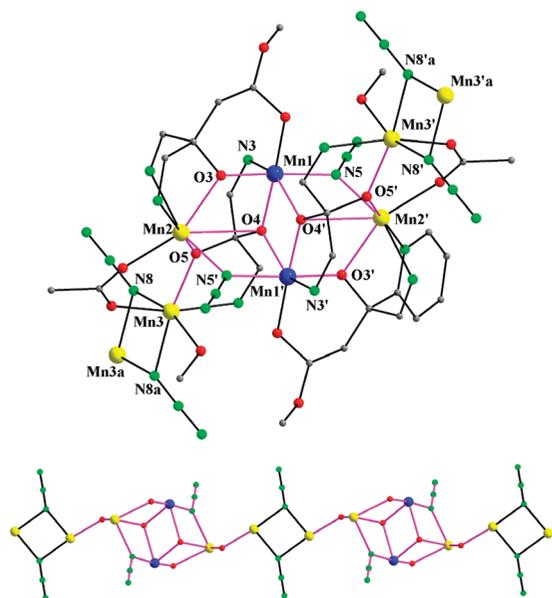


Figure 1. (Top) Labeled PovRay representation of the Mn_6 repeating unit of **1**. Only the N and two C atoms of the pyridine rings are shown. H atoms have been omitted for clarity. (Bottom) Section of the 1D chain. Color scheme: Mn^{II} , yellow; Mn^{III} , blue; O, red; N, green; C, gray. Primed, unprimed, a, and a' atoms are related by symmetry.

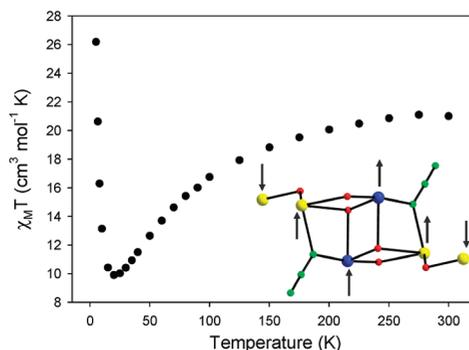


Figure 2. $\chi_{\text{M}}T$ vs T plot for complex **1** in a 1 kG field. Inset: Proposed spin alignments in the repeating Mn_6 unit that give its putative $S = 4$ ground state. Color scheme as in Figure 1.

latter becoming $\eta^1:\eta^1:\mu$ (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) calculations¹⁸ and the clear Jahn–Teller (JT) axial elongations ($\text{O4}'\text{—Mn1—N3}$) 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 $\text{Mn}\cdots\text{Mn}$ 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 (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 $\chi_{\text{M}}T$ vs T in Figure 2. $\chi_{\text{M}}T$ steadily decreases from 21.00 $\text{cm}^3 \text{K mol}^{-1}$ at 300 K to a minimum of 9.90 $\text{cm}^3 \text{K mol}^{-1}$ at 20.0 K and then rapidly increases to 26.19 $\text{cm}^3 \text{K mol}^{-1}$ at 5.0 K. The shape of the $\chi_{\text{M}}T$ 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 $[\text{Mn}_4(\mu_3\text{-OR})_2(\mu\text{-OR})_4]$ 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: $\text{C}_{56}\text{H}_{58}\text{N}_{20}\text{O}_{16}\text{Mn}_3$, 1596.84 g mol^{-1} , monoclinic $P2_1/n$, $a = 12.104(2)$ Å, $b = 20.330(4)$ Å, $c = 13.557(3)$ Å, $\beta = 100.317(4)^\circ$, $Z = 4$, $V = 3282.0(11)$ Å³, $d_{\text{calc}} = 1.679$ g cm^{-3} , $T = 173(2)$ K. Final $R1 = 4.67$ and $wR2 = 11.20\%$.

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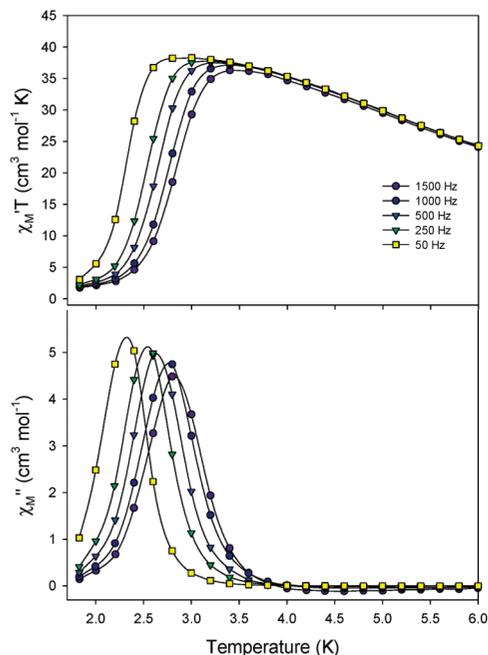


Figure 3. Plot of the in-phase (χ_M') (as $\chi_M'T$) and out-of-phase (χ_M'') ac susceptibility signals for complex **1**, measured in a 3.5 G field oscillating at the indicated frequencies.

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 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 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 large-cluster repeating units.^{10d,e,11b} In such cases, additional

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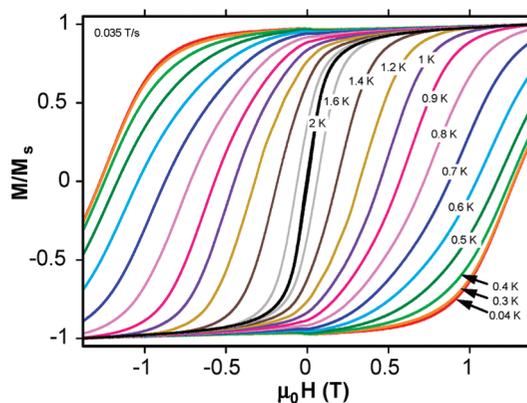


Figure 4. Magnetization (M) vs applied dc field (H) hysteresis loops for a single crystal of **1**·2MeOH at the indicated temperatures. The magnetization is normalized to its saturation value (M_s).

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 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} 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_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.

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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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