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Assembly of $[Mn^{II}{}_2Mn^{III}{}_2]$ $S = 9$ Clusters via Azido Bridges: a New Single-Chain Magnet

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S *Supporting Information*

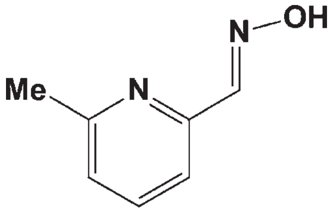
ABSTRACT: In the present work, we report a new manganese single-chain magnet built from tetranuclear $Mn^{II}{}_2Mn^{III}{}_2$ mixed-valence units linked by end-on azido and oximato bridges. All of the intra- and intercluster interactions involve end-on azido bridges, resulting in one ferromagnetic chain of ferromagnetic clusters with local ground state $S = 9$.

Research of molecule-based compounds that have a remnant magnetization in the absence of the external magnetic field is a growing topic in coordination chemistry since the discovery of the first single-molecule magnet (SMM) in 1993.[1] More recently, Gatteschi et al.[2] extended the study to one-dimensional (1D) systems (single-chain magnets, SCMs), which usually show greater relaxation times. Common features needed to obtain this kind of molecular or 1D system are a nonzero magnetic response at low temperature, anisotropic character, and well-isolation in the crystalline packing.

One of the major synthetic challenges in the design of molecular SMM or 1D SCM compounds is to reach an overall ferri- or ferromagnetic response. From the initial use of the azido ligand in 2001 in medium-nuclearity M_9 cluster chemistry[3] and the experimental proof that this ligand tends to end-on coordination modes (inducing ferromagnetic interactions) in cluster compounds, azido has been extensively employed in cluster syntheses.[4] During the past decade, the azido ligand contributed to reach giant spin $S = {}^{83}/_2$ Mn_{19} systems or several impressive high-nuclearity clusters containing more than 20 metallic centers in carboxylato, alkoxo, pyridylalkoxo, or salicyloximato chemistry, often exhibiting SMM properties.[5] In contrast, manganese/pyridyloximato/azido chemistry remains practically unexplored in spite of its potential possibilities and only some Mn_4 and Mn_6 units and one chain of Mn_4 units have been reported until now.[6]

The azido ligand also plays a significant role in the synthesis of SCM, as a bridge in conventional homospin chains like $[Co(bt)(N_3)_2]_n$ (bt = 2,2′-bithiazoline)[7] or as a linker in chains of clusters like $[Mn_4(hmp)_6(N_3)_2]_n(ClO_4)_{2n}$ [hmpH = 2-(hydroxymethyl)pyridine],[8a] $[Mn_3O(tbusalox)_3(N_3)(CH_3OH)_4]$ (tbusalox = 3,5-di-*tert*-butylsalicylaldoxime),[8b] $[Mn_6(N_3)_4(O_2CMe)_2(dpkd)_2(dpkme)_2(MeOH)_2]_n$ ($dpkd^{2-}$ and $dpkme^{2-}$ = diol derivatives of dipyridylketone),[8c] or $[Mn_6O_2(4\text{-}MeOsalox)_6(N_3)_2(MeOH)_4]$ (MeOsalox = 2-hydroxy-4-methoxysalicylaldoxime).[8d]

Following our previous work in metal oximato chemistry, we have centered our attention on the ligand 6-methylpyridine-2-carbaldehydeoxime, (6-Mepy)C(H)NOH, for which only one $Ni^{II}{}_9$ compound has been characterized.[9] In this work, we report the initial use of (6-Mepy)C(H)NOH in manganese chemistry describing the neutral 1D system $[Mn_4\{(6\text{-}Mepy)C(H)NO\}_4(N_3)_6]_n\cdot 2n Et_2O$ (**1**$\cdot 2Et_2O$).



Ligand (6-Mepy)C(H)NOH was synthesized by a conventional reaction of 6-methylpyridine-2-carboxaldehyde and hydroxylamime hydrochloride in a basic ($NaCH_3COO$) medium. Compound **1**$\cdot 2Et_2O$ was obtained in good yield by a reaction in a methanolic medium of $Mn(hfacac)_2\cdot 3H_2O$, (Mepy)C(H)NOH, and NaN_3 in a 1:1:2 ratio. After the resulting dark-brown solution was layered with diethyl ether, X-ray-quality prismatic crystals of **1**$\cdot 2Et_2O$ were obtained after 4 days. Synthesis can also be carried out starting from weakly coordinating anions as manganese perchlorate or triflate salts. The structure[10] of **1** can be envisaged as neutral chains of tetranuclear $Mn^{II}{}_2Mn^{III}{}_2$ rings (Figure 1) linked by means of double end-on azido bridges. The MnN_4O_2 trans-coordination environment around the trivalent Mn(1) atom is defined by four azido N atoms and two O atoms from bridging oximato groups. The Mn−N bond distances are similar [2.105(3) and 2.169(3) Å] and larger than the Mn−O(1a,b) bond distances of 1.908(3) Å. Additionally, the polyhedron around Mn(1) is a compressed octahedron along the O−Mn−O axis. The MnN_6 cis-coordination environment for the divalent Mn(2) atom is defined by the pyridinic N donors of two $6\text{-}MepyNO^-$ ligands, two N atoms from bridging oximato groups, and two azido N atoms that bridge Mn(2) with Mn(1) and Mn(1b). Bond distances range between 2.194(3) and 2.273(3) Å. The octahedron is strongly distorted, exhibiting trans and cis bond angles in the 149.6(1)−167.8(1)° and 73.3(1)−115.4(1)° ranges, respectively. Each neighbor Mn(1)/Mn(2) atom is bridged by one

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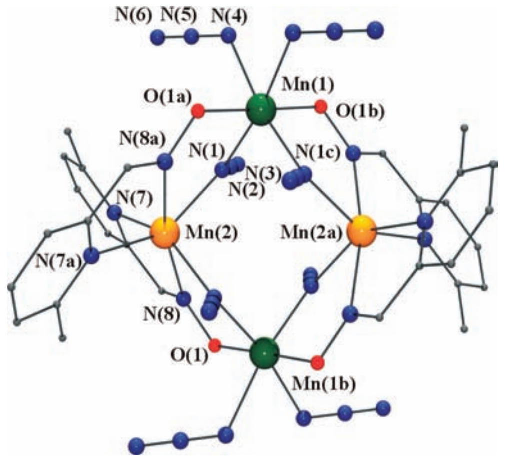

Figure 1. Partially labeled plot of the local Mn_4 units of **1**. Manganese color code: Mn^{II}, orange; Mn^{III}, dark green.

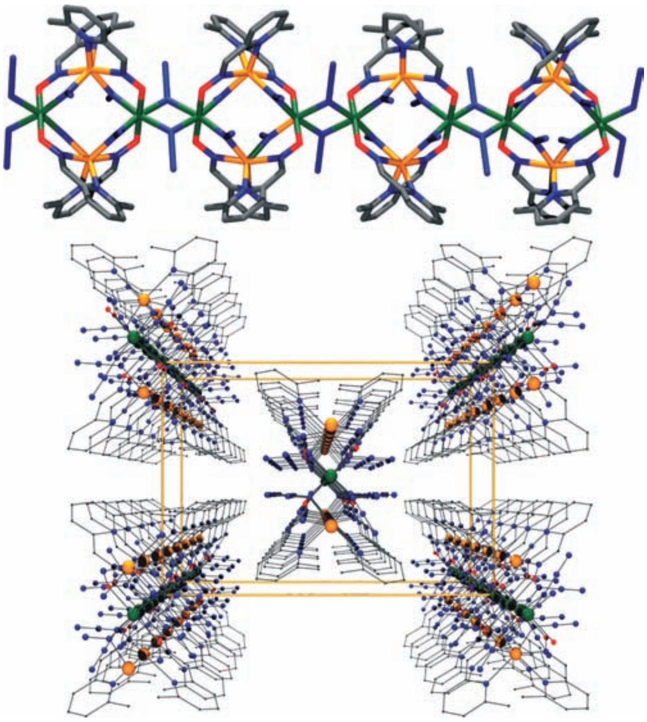

Figure 2. (Top) View of the chain of tetranuclear clusters linked by means of double azido bridges. (Bottom) Packing view along the [001] direction showing the well-isolated chains.

η^1:η^1:η^1:μ-(6-Mepy)C(H)N$\bar{\mathrm{O}}$ oximato and one end-on azido ligand (Figure 1). The Mn(1)−N(1)−Mn(2) bond angle is 117.1(1)°, resulting in an intraring Mn···Mn distance of 3.6669(8) Å. The Mn(1b)−O(1)−N(8)−Mn(2) torsion angle takes a value of 15.2(3)°.

It is noteworthy that the double azido−oximato bridge is not a recognizable fragment in previously reported manganese/azido/oximato clusters. The bridging ligands are placed above and below the plane defined by the four Mn atoms in a pseudotetrahedral arrangement as a result of the local symmetry. An important feature is that the two O−Mn(1)−O axis are quasi-orthogonal between them. Each tetranuclear unit is linked to two equivalent ones by means of double end-on azido bridges [Figure 2 (top)], with a Mn(1)−N(4)−Mn(1d) bond angle of 103.1(2)°, resulting in a Mn···Mn distance between adjacent tetramers of 3.397(1) Å. The chains are well-isolated and intrachain hydrogen bonds or $\pi-\pi$ stacking was not found [Figure 2 (bottom)].

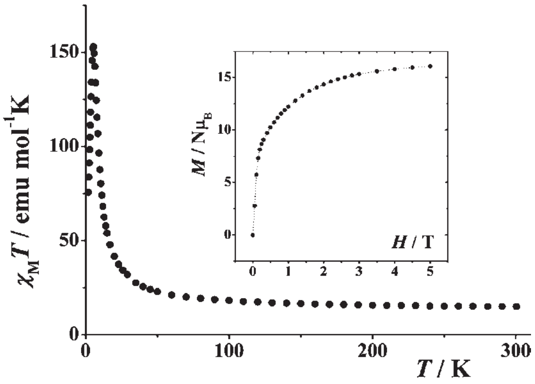

Figure 3. $\chi_M T$ product vs T plot for complex **1**. Inset: Magnetization measurement up to 5 T. Solid lines are guides for the eye.

Direct-current (dc) susceptibility measurements were performed between 300 and 2 K on powdered samples under external fields of 0.3 T (300−30 K) and 0.015 T (30−2 K) to avoid saturation effects. The room temperature $\chi_M T$ value is 15.00 cm^3 K mol^{-1}, which is slightly greater than the g = 2.00 value of 14.75 cm^3 K mol^{-1} expected for a $Mn^{II}{}_2Mn^{III}{}_2$ unit. On cooling, $\chi_M T$ increases gradually, reaching a maximum value of 153 cm^3 K mol^{-1} at 5.5 K. Below this temperature, $\chi_M T$ decreases to 75 cm^3 K mol^{-1} at 1.8 K (Figure 3). The continuous increase of the $\chi_M T$ product is only compatible with a system with ferromagnetic interactions inside the tetrameric units, and the maximum value of 153 cm^3 K mol^{-1}, clearly larger than the expected value for a ferromagnetic $Mn^{II}{}_2Mn^{III}{}_2$ ring (S = 9, 45.00 cm^3 K mol^{-1}), indicates ferromagnetic interactions between the tetrameric clusters.

These data support the 1D response of the system that magnetically can be described as a ferromagnetic chain of ferromagnetic rings with local ground state S = 9. Calculation of intracluster (assuming isolated clusters, $J_{\mathrm{intra}} \gg J_{\mathrm{inter}}$) or intercluster (assuming isolated Mn^{III} dimers, $J_{\mathrm{intra}} \ll J_{\mathrm{inter}}$) coupling constants using the high T susceptibility values was ambiguous, indicating that both constants contribute significantly to the global coupling (Figure S1 in the Supporting Information). Magnetization experiments at 2 K up to 5 T show a very fast magnetization ($M\mu_\beta$ = 7.3 under a field of only 0.15 T), suggesting that the stronger coupling may correspond to the interaction between Mn^{III} ions mediated by double azido bridges. When the external field is increased, the magnetization gradually reaches a value equivalent to 16 electrons under the maximum field. Relevant features for the field-cooled/zero-field-cooled (FC/ZFC) measurements or hysteresis cycle were not found, indicating a blocking temperature lower than 2 K (Figure S2 in the Supporting Information). Reduced magnetization experiments show a small gap at different fields, indicating moderate anisotropy of the ground state (Figure S3 in the Supporting Information).

The structural data and the dc magnetic response of **1** allow a description of the system as well-isolated ferromagnetic chains of S = 9 local spins, and then to probe the magnetization dynamics

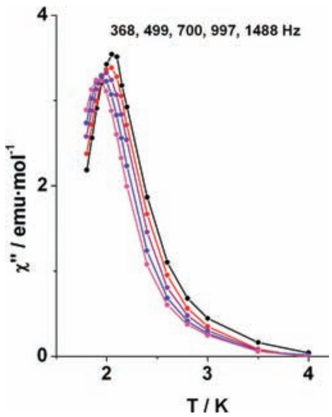

Figure 4. Plot of the out-of-phase (χ_M'') ac susceptibility signals for complex **1**. Measurements were performed under an oscillating field of 4 G at the indicated frequencies.

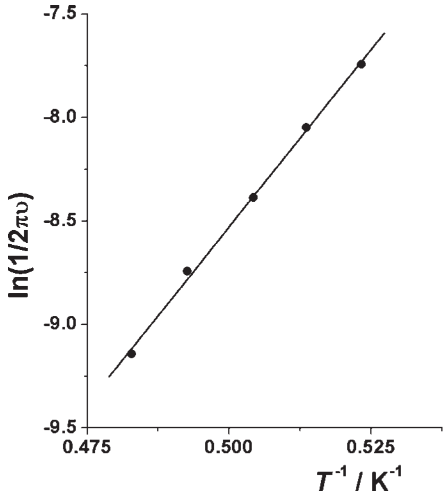

Figure 5. Peak temperatures of χ_M'' ac susceptibility measurements fitted to the Arrhenius law for a complex.

of **1**, alternating-current (ac) experiments were performed at 1.8−10 K under an oscillating field of 4 G. Susceptibility measurements show complete peaks above 1.8 K for frequencies in the 350−1500 Hz range and only the tail of the curves for low frequencies (Figure 4). Debye treatment of the frequency dependence of ac returns an α value of 0.06 (Figure S4 in the Supporting Information). The shift of the peak temperature (T_p) is given by the parameter $F = (\Delta T_p/T_p)/\Delta(\log \omega) = 0.14$, which lies in the expected range for a SCM ($0.1 < F < 0.3$), discarding spin-glass behavior.[11]

A fit of the Arrhenius plot from the ac χ_M'' vs T data (Figure 5) gives $\Delta E = 24$ K and $\tau_0 = 7.3 \times 10^{-12}$ s, where ΔE is the energy barrier for the magnetization relaxation and τ_0 is the preexponential factor. 1D Ising chain behavior is also confirmed by the linear fit of the linear region of $\ln(\chi' T)$ vs T^{-1}, which returns an energy gap $\Delta_\xi = 7.7$ K (Figure S5 in the Supporting Information).[12]

The relatively low barrier found for **1** in spite of the ferromagnetic interactions along the chain and the high local spins should be attributed to the unfavorable alignment of the easy axis of the anisotropic centers Mn(1)/Mn(1b). Compound **1** provides a new example of the relevant versatility of the azido ligand in the syntheses of high-spin molecular or extended systems, and current efforts to obtain related chains with a series of (*R*)-pyridyloximato ligands are in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data for complex $\mathbf{1}\cdot 2Et_2O$ in CIF format, a Cole−Cole plot, and FC/ZFC measurement, a reduced magnetization plot, an Argand plot, and a linear fit of the semilog $\chi_M'T$ vs $1/T$ for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystal data for $\mathbf{1}\cdot Et_2O$: $C_{14}H_{14}Mn_2N_{13}O_2\cdot C_4H_{10}O$ (580.38), orthorhombic, *Ibam*, $a = 20.391(2)$ Å, $b = 13.470(1)$ Å, $c = 17.911(2)$ Å, $V = 4919.5(7)$ Å^3, $Z = 8$, $T = 100(2)$ K, λ(Mo Kα) = 0.710 73 Å, 32 014 reflections collected, 2510 unique ($R_{int} = 0.040$), R1 = 0.0479, wR2 = 0.1361. CCDC deposition number 802314.

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