

Old ligands with new coordination chemistry: A Mn₁₇Na cluster bearing triethanolamine and azide groups and exhibiting slow magnetization relaxation

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ABSTRACT

The combination of azide, carboxylate and triethanolamine ligands in higher oxidation state Mn cluster chemistry has yielded a new heptadecanuclear, mixed-valence (II, III, IV) compound with fairly large S and D values, and frequency-dependent out-of-phase (χ''_M) signals, characteristics of the superparamagnetic-like slow relaxation of an SMM.

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Single-molecule magnets (SMMs) are individual molecules that function as single-domain nanoscale magnetic particles [1]. A SMM derives its properties from a combination of a large ground-state spin (S) value and an easy-axis type of magnetoanisotropy (negative zero-field splitting parameter, D), which results in a significant energy barrier to reversal of the magnetization vector, experimentally observed by the appearance of frequency-dependent out-of-phase (χ''_M) AC signals and magnetization hysteresis. Such species also straddle the classical/quantum interface by displaying not just classical magnetization hysteresis but also quantum tunnelling of magnetization (QTM) [2] and quantum phase interference [3]. Thus, SMMs represent a molecular ('bottom-up') route to nanoscale magnetism [4], with potential technological applications in information storage and spintronics at the molecular level [5a], and use as quantum bits (qubits) in quantum computation [5b]. The upper limit to the barrier (U) is given by $S^2|D|$ or $(S^2 - 1/4)|D|$ for integer and half-integer S , respectively; in practice, QTM through upper regions of the barrier makes the true or effective barrier (U_{eff}) less than U .

Although complexes displaying SMM behavior are known for several metals, manganese cluster chemistry has been the most fruitful source to date giving a wide range of Mn_{*x*} nuclearities, with x taking values up to 84, the latter being still the largest known SMM [6]. For these reasons, and more, we are developing new synthetic methods to Mn clusters of various nuclearities and structural types. In particular, we have recently started a program aiming at the investigation of the coordination affinity of N₃⁻ ion in higher oxidation state Mn cluster chemistry and in reactions with several

families of versatile chelates, such as pyridyl or non-pyridyl alcohols or poly-alcohols and pyridyl oximes [7]. From a magnetic viewpoint, the N₃⁻ ion bridging in the 1,1-fashion (end-on) is one of the strongest ferromagnetic mediators in molecular magnetism for a wide range of M–N–M angles, while triethanolamine (teaH₃) chelate, for instance, exhibits a large coordinating multifunctionality with metal centers; thus, their amalgamation provided an attractive route to new high-nuclearity/high-spin Mn clusters and SMMs [7].

The reaction of Mn(ClO₄)₂ · 6H₂O, NaO₂CCMe₃, teaH₃, NEt₃, and NaN₃ in a 1:2:1:1:2 molar ratio in MeCN/DMF (2:1, v/v) gave a dark brown solution from which were subsequently isolated dark brown crystals of [Mn₁₇NaO₁₀(OH)₂(N₃)₃(O₂CCMe₃)₁₃(tea)₃(teaH)(DMF)] (1) in 45% yield.¹

The structure of 1 (Mn^{II}₄Mn^{III}₁₂Mn^{IV})₂ consists of a Mn₁₇Na cage-like cluster (Fig. 1) with an irregular structural conformation. The [Mn₁₇Na(μ₄-O)₈(μ₃-O)₂(μ₃-OH)₂(μ-OH)₂(μ₃-N₃)]²⁵⁺ core comprises seven [Mn₄(μ₄-O²⁻)] and a [Mn₃Na(μ₄-O²⁻)] tetrahedra fused together and linked to two adjacent [Mn₃(μ₃-O²⁻)] and a [Mn₂Na(μ₃-OH⁻)] triangles by sharing common Mn vertices. Alternatively, the core of 1 could be described as a central [Mn₃Na(μ₄-O²⁻)] tetrahedron fused to two [Mn₄(μ₃-O²⁻)₄] and

¹ Elemental Anal. Calc. for C₉₂H₁₇₅Mn₁₇NaN₁₄O₅₁ (1): C, 34.00; H, 5.43; N, 6.03. Found: C, 34.22; H, 5.46; N, 6.04%. Selected IR data (KBr): 3446mb, 2962m, 2869w, 2071s, 1653m, 1560vs, 1482m, 1411vs, 1362m, 1223m, 1075m, 906m, 787w, 693m, 660mb, 599m, 556w, 444w cm⁻¹.

² Crystal structure data for 1 · 5MeCN: C₁₀₂H₁₈₈Mn₁₇NaN₁₉O₅₁, $M_r = 3453.68$, orthorhombic, space group $P2_12_12_1$, $a = 17.463(3)$ Å, $b = 18.144(3)$ Å, $c = 46.054(7)$ Å, $V = 46.054(7)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.572$ g cm⁻³, $T = 173(2)$ K, 55542 reflections collected, 19027 unique ($R_{\text{int}} = 0.1192$), $R_1 = 0.0972$ and $wR_2 = 0.2053$, using 11831 reflections with $I > 2\sigma(I)$.

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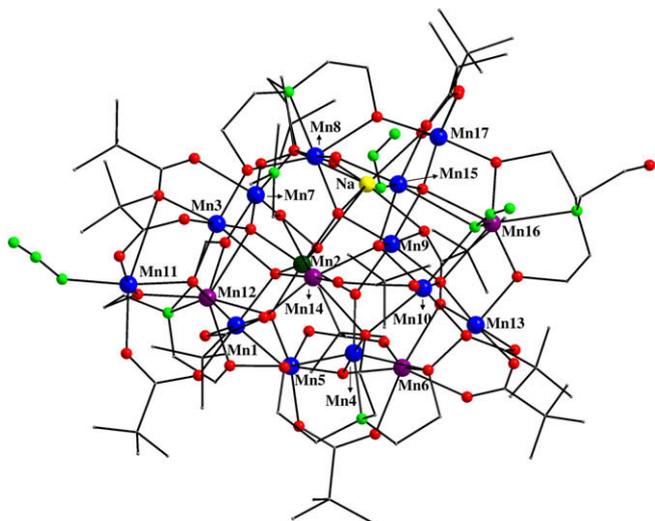


Fig. 1. Molecular structure of complex **1**. H atoms have been omitted for clarity. Color scheme: Mn^{II} purple; Mn^{III} blue; Mn^{IV} olive; Na yellow; O red; N green; C grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[Mn₄(μ₃-O²⁻)₃(μ₃-N₃)] cubane subunits at common atoms Mn2 and Mn9, respectively. All μ₃-O²⁻ ions in each cubane subunits convert to a μ₄ mode and bridge seven adjacent Mn atoms, three of which (Mn2,5,7) are fused to the corresponding triangular subunits. The three tea³⁻ groups are bound to up to six Mn atoms, acting as η³:η¹:η²:η³:μ₆, η²:η¹:η³:η²:μ₅ and η²:η¹:η²:η²:μ₃ ligands, the μ₆ mode being seen for a first time in the coordination chemistry of this group, while the only teaH²⁻ group is bridging under the η²:η¹:η²:μ₃ mode. Peripheral ligation about the core is provided by ten η¹:η¹:μ, two η¹:η²:μ and an η²:η²:μ₄ Me₃CCO₂⁻ groups, as well as two terminal N₃⁻ ions and a terminal DMF molecule. All Mn and Na atoms are near-octahedral, except five-coordinate Mn5 and seven-coordinate Mn12, which are square pyramidal ($\tau = 0.01$ [8]) and distorted pentagonal bipyramidal, respectively. The Mn^{II}/Mn^{III}/Mn^{IV}/Na^I oxidation states were established from the metric parameters, BVS calculations³ [9], and the presence of Jahn–Teller (JT) distortions at octahedral Mn³⁺. The protonation level of O²⁻, OH⁻, and OR⁻ groups was also confirmed by BVS calculations [9]. There are no significant intermolecular interactions of any kind, only strong intramolecular H-bonds between bridging OH⁻ and DMF and Me₃CCO₂⁻ groups, respectively.

While the number of polynuclear complexes of 3d metals at intermediate oxidation states continues to grow rapidly, some nuclearities remain rare. Heptadecanuclear 3d metal complexes are particularly rare [10]; **1** is only the second Mn₁₇ cluster ever reported [10a], and the first with such a closed-like structural topology.

Solid-state DC (direct current) magnetic susceptibility (χ_M) data for complex **1** were collected in the temperature range 5.0–300 K in an applied field of 1 kG (0.1 T). The data are plotted as $\chi_M T$ versus T in Fig. 2, and clearly indicate a relatively large ground-state spin (S) value. $\chi_M T$ for **1** steadily decreases from 44.74 cm³ K mol⁻¹ at 300 K to reach a plateau of ~ 35.50 cm³ K mol⁻¹ at 20–40 K, before further dropping to 33.49 cm³ K mol⁻¹ at 5.0 K; the latter decrease at the lowest temperatures is assigned to Zeeman effects, zero-field splitting and/or weak intermolecular interactions. The overall shape of the $\chi_M T$ versus T curve and the existence of the

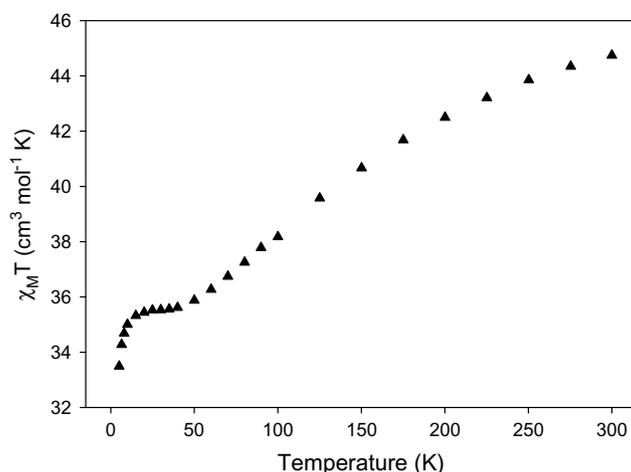


Fig. 2. $\chi_M T$ vs. T plot for **1** in a 1 kG field.

20–40 K plateau region are indicative of predominant antiferromagnetic exchange interactions within **1** and a well-isolated ground state S , respectively. The 20–40 K value is consistent with an $S = 17/2$ ground state and a g value slightly less than 2.0, as expected for a Mn^{II,III,IV} complex; the spin-only ($g = 2$) value for an $S = 17/2$ state is 40.38 cm³ K mol⁻¹.

In order to confirm the ground state of **1**, magnetization (M) data were collected in the 0.1–1.0 T and 1.8–10.0 K ranges, and these are plotted as $M/N\mu_B$ versus H/T in Fig. 3. We used only low field data (≤ 1.0 T) to preclude problems from low-lying excited states, which are expected for high-nuclearity clusters with a high density of spin states and/or when Mn^{II} ions are present, which give weak exchange interactions. The data were fit by matrix-diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Fig. 3) gave $S = 17/2$, $g = 1.85$ and $D = -0.22$ cm⁻¹; alternative fits with $S = 15/2$ or $19/2$ were rejected because they gave unreasonable values of g and D . We conclude that **1** has ground state of $S = 17/2$, respectively. This was further confirmed by AC (alternating current) susceptibility experiments.

As we have described before on multiple occasions [11], AC susceptibility studies in the 1.8–15 K range with a 3.5 G AC field oscil-

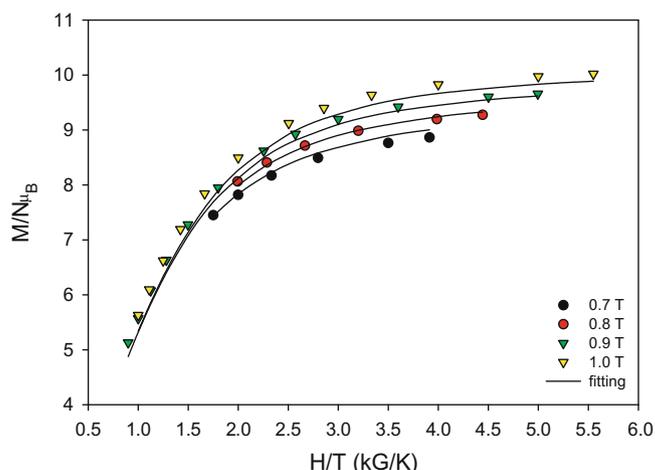


Fig. 3. Magnetization (M) vs. field (H) and temperature (T) data, plotted as reduced magnetization ($M/N\mu_B$) vs. H/T , for complex **1** at applied fields of 0.7–1.0 T and in the 1.8–10 K temperature range. The solid lines are the fit of the data; see the text for the fit parameters.

³ Bond-valence sum (BVS) calculations for the Mn ions of **1** gave values of 1.77–1.94 for Mn²⁺ ions, 2.77–3.06 for Mn³⁺ ions, 4.03 for Mn⁴⁺ ion and 1.20 for Na⁺ ion. BVS calculations for selected oxygen atoms in **1** gave values of 1.72–2.07 for O²⁻, 0.90–1.01 for OH⁻, 1.75–1.93 for RO⁻, and 1.05–1.23 for ROH.

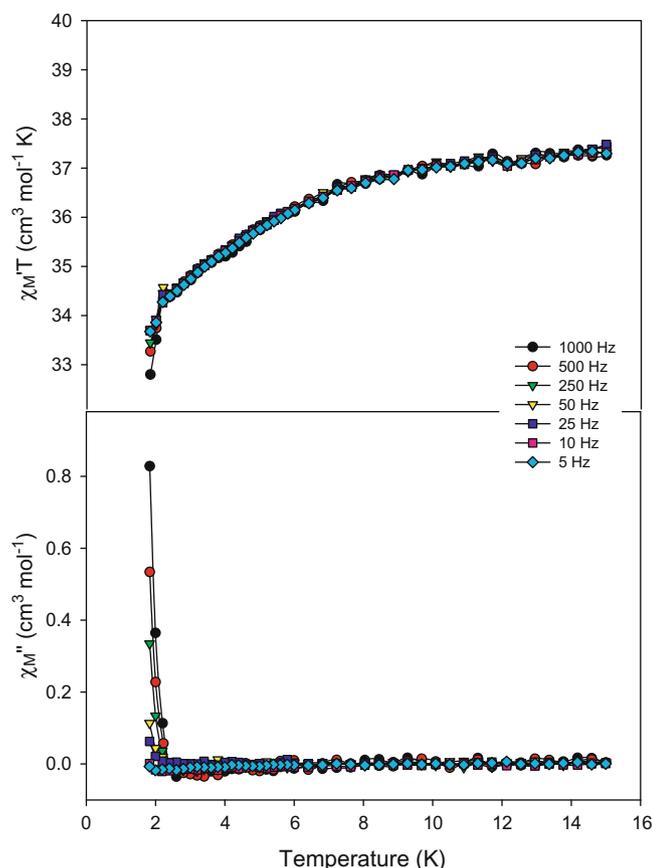


Fig. 4. Plots of the in-phase (χ'_M) as $\chi'_M T$ (top), and out-of-phase (χ''_M) AC magnetic susceptibilities vs. T in a 3.5 G field oscillating at the indicated frequencies for complex **1**.

lating at 5–1000 Hz are a powerful complement to DC studies for determining the ground state of a system, because they preclude any complications arising from the presence of a DC field and/or low-lying excited states. For **1**, the in-phase (χ'_M) AC signal, shown as $\chi'_M T$ in Fig. 4 (top), is only slightly decreasing with decreasing temperature in the 8–15 K region; extrapolation of the data above 8 K (to avoid the effects of intermolecular interactions at lower temperatures) down to 0 K gives $\sim 36.5 \text{ cm}^3 \text{ K mol}^{-1}$, indicating an $S = 17/2$ ground state with $g \sim 1.95$, in good agreement with the DC magnetization fits.

The $S = 17/2$ ground state and the negative D value suggested that **1** might be SMM. The upper limit to the barrier is $U = (S^2 - 1/4)|D| = 15.70 \text{ cm}^{-1} = 22.59 \text{ K}$, but the true, effective barrier (U_{eff}) will be significantly less due to QTM. At temperatures $< 3.0 \text{ K}$, frequency-dependent tails of out-of-phase (χ''_M) AC susceptibility signals for **1** were observed (Fig. 4, bottom) whose maxima lie below the operating minimum temperature of our SQUID instrument. Such signals are an indication of the superparamagnetic-like slow relaxation of an SMM. To confirm whether **1** is a SMM and shows hysteresis loops, the diagnostic property of a magnet, single-crystal magnetic studies are required to be performed at low enough temperatures using the micro-SQUID apparatus [12]. Such studies are currently in progress and the corresponding results will be reported in due course.

In summary, the combination of azide, carboxylate and teaH_3 ligands in Mn cluster chemistry has yielded an unprecedented heptadecanuclear, mixed-valence (II, III, IV) cage-like molecule with a fairly large $S = 17/2$ ground state and an appreciably large and negative D value. As a result, out-of-phase (χ''_M) AC tails of signals have been observed, indicative of the superparamagnetic-like slow relaxation of an SMM. Finally, the combined structural and magnetic results reported herein continue to emphasize how extensive is the ability of Mn chemistry to satisfy a variety of different tastes.

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Appendix A. Supplementary data

CCDC 700136 contains the supplementary crystallographic data for **1** · 5MeCN. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.10.032.

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