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A new Mn_{25} single-molecule magnet with an $S = 61/2$ ground state arising from ligand-induced 'spin-tweaking' in a high-spin molecule

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Abstract

Reactivity studies of a $[Mn_{25}]^{2+}$ cage of full formula $[Mn^{II}_6Mn^{III}_{18}Mn^{IV}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6]^{2+}$ (**1**) involving replacement of azide groups with hmp^- ones have led to a new, isostructural $[Mn_{25}O_{18}(OH)(OMe)(hmp)_6(pdm)_6(pdmH)_6]^{8+}$ (**2**) cluster with new and impressive magnetic properties. The successful ligand (hmp^-)-induced structural distortion of the preformed Mn_{25} cluster (**1**) with an $S = 51/2$ ground-state causes the ground-state spin to increase remarkably (~20%) to $S = 61/2$. Hysteresis loops are seen below ~1.0 K whose coercivities increase with increasing sweep rate and with decreasing temperature. This confirms **2** to be an SMM, possessing one of the highest S values ever reported.

Keywords: Cluster compounds; High-spin Molecules; Manganese; N, O ligands; Single-molecule magnets

Polynuclear metal clusters containing paramagnetic metal ions are of intense interest for several reasons, and one of these is the possibility that they might possess high-spin (S) ground states and a magnetoanisotropy of the easy-axis or Ising-type (negative zero-field splitting parameter, D). Such molecules often have a significant energy barrier (versus kT, where k is the Boltzmann constant) to reversal of the magnetization (magnetic moment) vector, and thus at low enough temperatures the magnetization is blocked and the molecules function as nanoscale magnetic particles [1]. In addition, they clearly straddle the classical/quantum interface, displaying not just the magnetization hysteresis but also the quantum properties of quantum tunneling of the magnetization (QTM) [2] through the anisotropy barrier, and quantum phase interference [3]. Such single-molecule magnets (SMMs) represent a molecular, or 'bottom-up', route to nanoscale magnetism [4], with potential applications in information storage and quantum computing. The upper limit to the barrier (U) to magnetization relaxation is given by $S^2|D|$ or $(S^2 - 1/4)|D|$ for integer and half-integer spin, respectively; in practice, the actual or effective barrier (U_{eff}) is less than U because of QTM through the anisotropy barrier via higher lying M_s levels of the spin S manifold.

The synthesis of new high-spin molecules is thus of great importance if new SMMs are to be discovered. Large S values can result from ferromagnetic (or ferrimagnetic) exchange interactions between the metal centers, and/or from competing antiferromagnetic interactions in certain M_x topologies that prevent (frustrate) the preferred spin alignments that would yield low-spin species. Nevertheless, it is difficult to achieve a rational synthesis of a high-spin species from simple reagents, and even then there is the danger that the anisotropy will be too low to either give an SMM, or to give one with a reasonable barrier [5].

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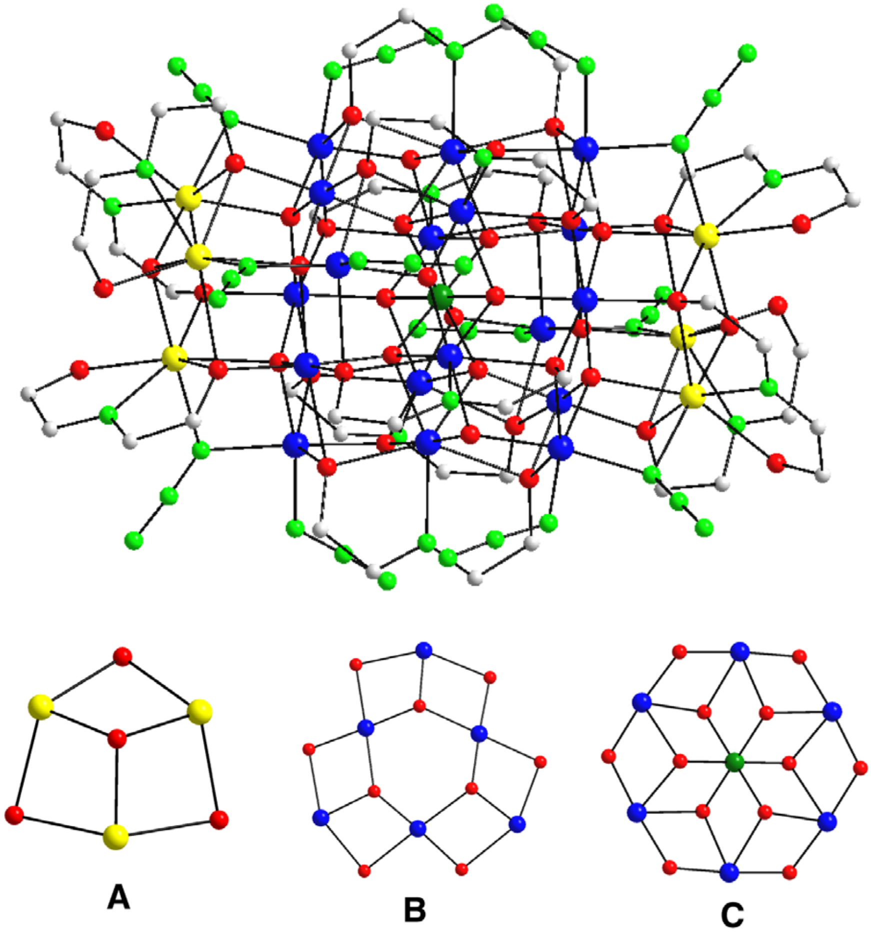
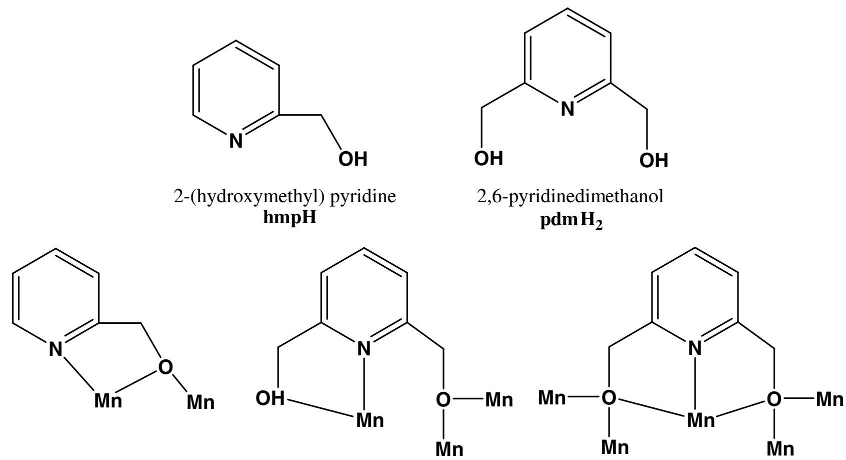


Fig. 1. Structure of the cation of **1** (top) and the three types of constituent layers of its core (bottom). Color code: Mn^{II} yellow, Mn^{III} blue, Mn^{IV} olive, O red, N green, C gray. H atoms have been omitted for clarity. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

An alternative approach to new high-spin molecules pertinent to the present report is to start with a preformed, high-spin molecule and then perturb it in some way, without major structural change, in order to modify the constituent exchange parameters and possibly alter the ground state (hopefully to a larger value rather than a smaller one). While this is often stated in the literature as an objective, it has yet to be realized. In the present work, we show that it is indeed possible to significantly modify the ground state spin of a complicated, already high-spin molecule without significant core structural change by controlled ligand substitution within the peripheral ligation about the magnetic core. Specifically, we show that ligand-induced tweaking of a SMM with $S = 51/2$ causes the ground state to increase to $S = 61/2$ without unduly affecting the anisotropy. As a result, the product is a new SMM.

The present Short Communication deals with the Mn_{25} SMM complex of full formula $[Mn^{II}_6Mn^{III}_{18}Mn^{IV}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6]$ X_2 [(**1**); X = Cl or N_3; $pdmH_2$ is 2,6-pyridinedimethanol]. The $X = Cl^-$ salt was the original one prepared [5a] but the present work has been carried with the $X = N_3^-$ salt, available in a much better yield of 75% from a related procedure. The Mn_{25} cation of **1**[1] has a barrel-like cage structure with twelve μ_4-O^{2-}, six μ_3-O^{2-}, and two μ_3-OH^- ions holding the core together (Fig. 1, top). The peripheral ligation is provided by chelating/bridging pdm^{2-}/$pdmH^-$ and both terminal and end-on bridging N_3^- groups. The core may be dissected into five layers of three types with an ABCBA arrangement (Fig. 1, bottom). Layer A is a Mn^{II}_3 triangular unit with a capping μ_3-OH^- ion; layer B is a Mn^{III}_6 triangle comprising three corner-sharing Mn^{III}_3 triangles; and layer C is an Anderson-type Mn^{III}_6 hexagon with a central Mn^{IV} ion. Each layer is held together and linked to its neighboring layers by a combination of O^{2-}, OR^-, and/or N_3^- bridges.

[1] Crystal structure data for $\mathbf{1}\cdot 10MeCN$: $C_{104}H_{122}Mn_{25}N_{64}O_{44}$, $M_r = 4345.98$, triclinic, space group $P\bar{1}$, $a = 15.9646(12)$, $b = 16.5361(13)$, $c = 17.3483(14)$ Å, $\alpha = 97.895(2)$, $\beta = 101.094(1)$, $\gamma = 117.345(1)°$, $V = 3855.8(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.085$ g cm^{-3}, $T = 173(2)$ K, 21329 reflections collected, 13437 unique ($R_{int} = 0.0335$), $R_1 = 0.0519$ and $wR_2 = 0.1546$, using 13437 reflections with $I > 2\sigma(I)$. Crystal structure data for $\mathbf{2}\cdot xMeCN\cdot yMeOH$: $C_{121}H_{130}Mn_{25}N_{24}O_{74}Cl_6$, $M_r = 4690.67$, rhombohedral, space group $R\bar{3}c$, $a = 22.0975(9)$, $c = 69.811(5)$ Å, $V = 29522(3)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.495$ g cm^{-3}, $T = 173(2)$ K, 16378 reflections collected, 4080 unique ($R_{int} = 0.0756$), $R_1 = 0.0674$ and $wR_2 = 0.1860$, using 4080 reflections with $I > 2\sigma(I)$.



Scheme 1. The pyridyl–alcohol ligands discussed in the text (top), and the crystallographically established coordination modes of the hmp^{-}, $pdmH^{-}$, and pdm^{2-} ligands present in complexes **1** and **2** (bottom).

The $[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6]^{2+}$ cation has an $S = 51/2$ ground state, and we undertook the challenge of tweaking this spin value without core structural change.

We have extensive experience with pyridine-based alkoxide ligands in Mn cluster chemistry, and have seen that the anion of 2-(hydroxymethyl)pyridine (hmp^{-}), like $pdmH^{-}$ and pdm^{2-} (Scheme 1), is a versatile N,O-chelating and bridging ligand that often yields ferromagnetic coupling between metal atoms [5b,6]. We thus targeted replacement of the twelve azide ions of **1** by six hmp^{-} groups, and this ultimately proved successful.

The reaction of **1** ($X = N_3^{-}$), Na(hmp), and $NaClO_4 \cdot H_2O$ in a 1:6:6 molar ratio in MeCN/MeOH[2] gave a dark brown solution from which were subsequently isolated crystals of $[Mn_{25}O_{18}(OH)(OMe)(hmp)_6(pdm)_6(pdmH)_6](N_3)_2(ClO_4)_6 \cdot x\text{MeCN} \cdot y\text{MeOH}$ ($\mathbf{2} \cdot x\text{MeCN} \cdot y\text{MeOH}$) in 63% yield. The crystal structure[1] shows the core of **2** to be isostructural with that in **1**; Mn oxidation states and the protonation levels of all O atoms in the molecule were established by Mn and O bond valence sum (BVS) calculations [7],[3] inspection of metric parameters, and detection of Mn^{III} Jahn-Teller (JT) elongation axes. The main difference is that the twelve bound azides of **1** are now replaced by six $\eta^1:\eta^2:\mu_2$ hmp^{-} ligands in **2** and also a μ_3-OH^{-} group of **1** is substituted by a μ_3-MeO^{-} ligand in **2** (Fig. 2). As a result, all intra- and inter-layer bridges, as well as all M_2 pairwise exchange interactions, are now through oxo-atoms, and there are consequently small metric differences between the cores of **1** and **2**.[4] There will thus some changes expected to many of the exchange interactions in the molecule. Considering that the ground state of such a large molecule consisting of both ferro- and antiferromagnetic interactions will be acutely sensitive to the relative magnitudes of the multiple exchange interactions, many of them competing, it was considered likely that the ground state S value might change, and this was therefore explored by detailed magnetochemical measurements.

Solid-state DC magnetic susceptibility (χ_M) data for dried $\mathbf{2} \cdot 4\text{MeCN}$ were collected in the temperature range 5.0–300 K in an applied field of 1 kG (0.1 T). $\chi_M T$ steadily increases from 120.20 $cm^3\ mol^{-1}$ K at 300 K to a maximum of 457.42 $cm^3\ mol^{-1}$ K at 20 K, before dropping to 401.94 $cm^3\ mol^{-1}$ K at 5.0 K (Fig. 3). The spin-only ($g = 2$) value for a non-interacting $[Mn^{II}_6Mn^{III}_{18}Mn^{IV}]$ unit is 82.125 $cm^3\ mol^{-1}$ K, indicating at least some ferromagnetic exchange interactions within **2**, and the 20 K data strongly suggest a very large ground-state spin (S) value. The low temperature data are consistent with an S in the 59/2 to 65/2 range, depending on the g value, significantly greater than the $S = 51/2$ of **1**.

In order to determine the ground state of $\mathbf{2} \cdot 4\text{MeCN}$, 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. 4. We used only low field data ($\leqslant$1.0 T), as we previously did for **1**, to avoid problems associated with M_s levels from excited states with higher S values crossing with the ground state, which would lead to an erroneously high value for the ground-state S. The data were fit by matrix-diagonalization to a model that

[2] It is pertinent to ask whether the Mn_{25} core structure stays intact in the MeCN/MeOH solvent used for the ligand substitution. Although we cannot answer this directly on the present system because of its complexity, we know from experience on related, higher symmetry Mn clusters (e.g. Mn_{12}, Mn_4, etc.), which we can study by NMR, that systems with higher average oxidation states and lots of oxide bridges retain their structures in solution. Compound **2** is one such molecule. Also the fact that the product is indeed of the same core structure as the starting material supports this in the present case.

[3] Bond-valence sum (BVS) calculations for Mn^{II}, Mn^{III} and Mn^{IV} ions of **2** gave oxidation state values of 1.94 (Mn^{II}), 2.88–2.99 (Mn^{III}) and 4.18 (Mn^{IV}) and for the oxygen atoms of O^{2-}, OH^{-}, hmp^{-}, $pdmH^{-}$, pdm^{2-} values of 1.84–2.03 (O^{2-}), 1.16–1.17 (OH^{-}, OMe^{-}, OR^{-}).

[4] A detailed comparison will be provided in the full paper of this work.

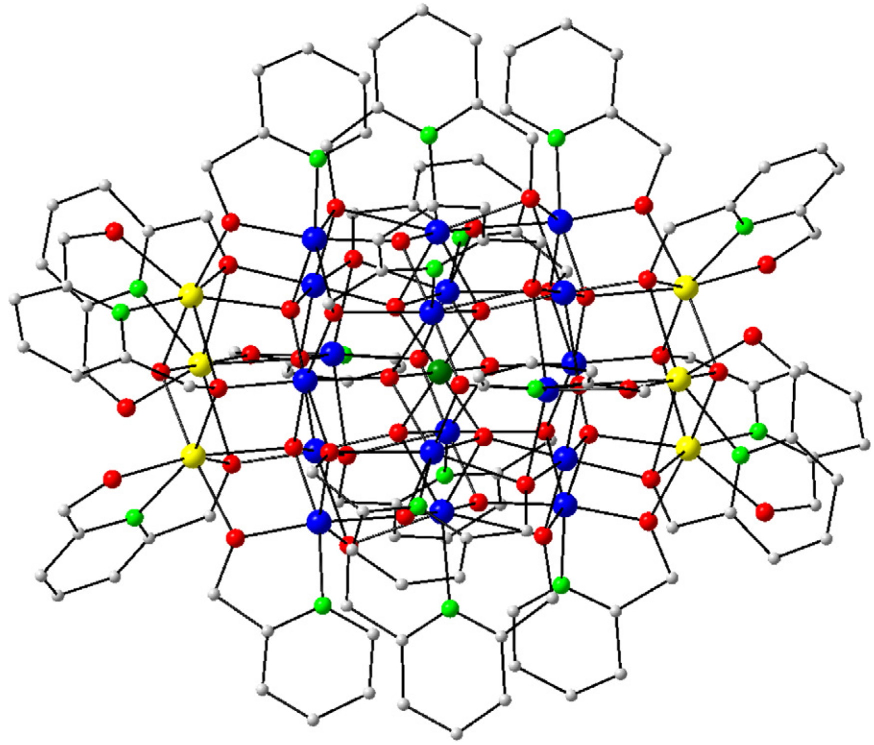


Fig. 2. Structure of the cation of **2**. Color code: Mn^{II} yellow, Mn^{III} blue, Mn^{IV} olive, O red, N green, C gray. H atoms have been omitted for clarity. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

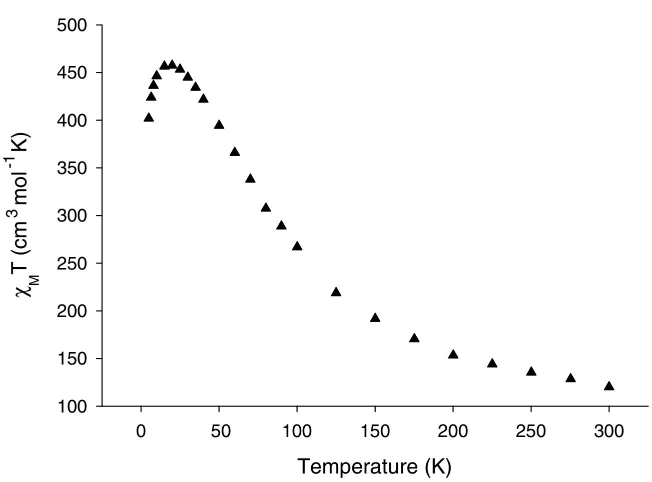


Fig. 3. $\chi_M T$ vs. T plot for complex $\mathbf{2} \cdot 4MeCN$ in a 1 kG field.

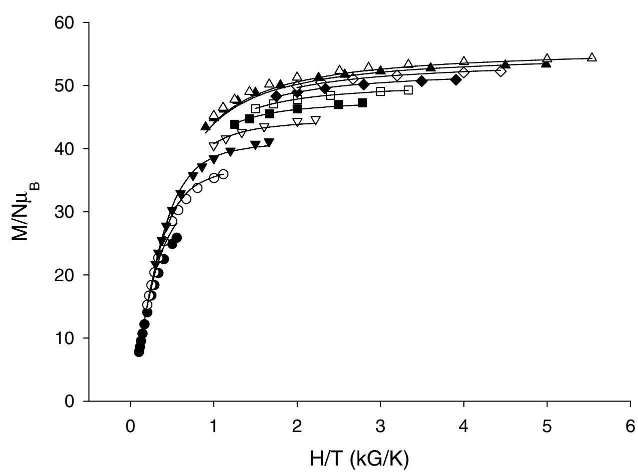


Fig. 4. Plot of reduced magnetization ($M/N\mu_B$) vs. H/T for $\mathbf{2} \cdot 4MeCN$ in the temperature range 1.8–10 K and in fields of 0.1 T (●), 0.2 T (○), 0.3 T (▼), 0.4 T (▽), 0.5 T (■), 0.6 T (□), 0.7 T (◆), 0.8 T (◇), 0.9 T (▲), and 1.0 T (△). Solid lines are the fit; see the text for the fitting parameters.

assumes only the ground state is populated, includes axial zero-field splitting ($D\widehat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Fig. 4) gave $S = 61/2$, $g = 1.92(1)$ and $D = -0.0120(1)$ cm^{-1}. The fits for $S = 59/2$, 63/2, and 65/2 were inferior, with best-fit parameters of $g = 1.98(1)/D = -0.0128(1)$ cm^{-1}, $g = 1.86(1)/D = -0.0113(1)$ cm^{-1}, and $g = 1.79(1)/D = -0.0106(1)$ cm^{-1}, respectively. We conclude that **2** has a ground state of $S = 61/2 \pm 1$.

Confirmation of the ground state S of $\mathbf{2} \cdot 4MeCN$ was obtained by alternating current (ac) susceptibility experiments. Ac susceptibility studies use no dc field and thus are an excellent complementary tool for determining S by avoiding potential complications from a large dc field. The in-phase susceptibility (χ'_M) for $\mathbf{2} \cdot 4MeCN$ is shown as $\chi'_M T$ versus T in Fig. 5, and extrapolation of the $\chi'_M T$ signal to 0 K from above ~8 K (to avoid the effects of intermolecular interactions at lower temperatures) gives a value of 440–470 cm^3 mol^{-1} K, consistent with the dc data

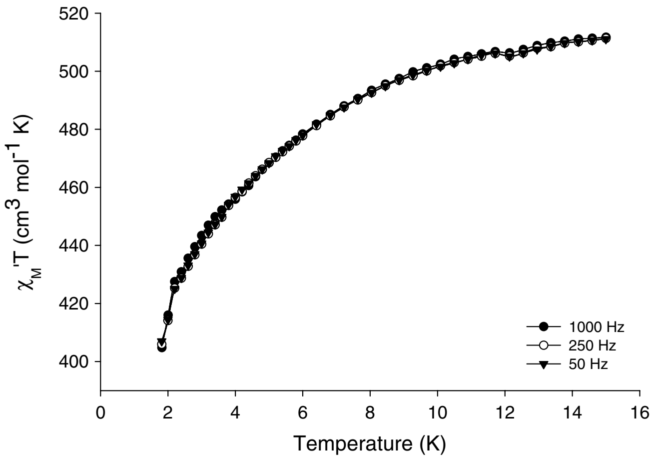


Fig. 5. In-phase ac susceptibility ($\chi_M'T$) measurements of complex **2** · 4MeCN measured below 15.0 K at the indicated frequencies.

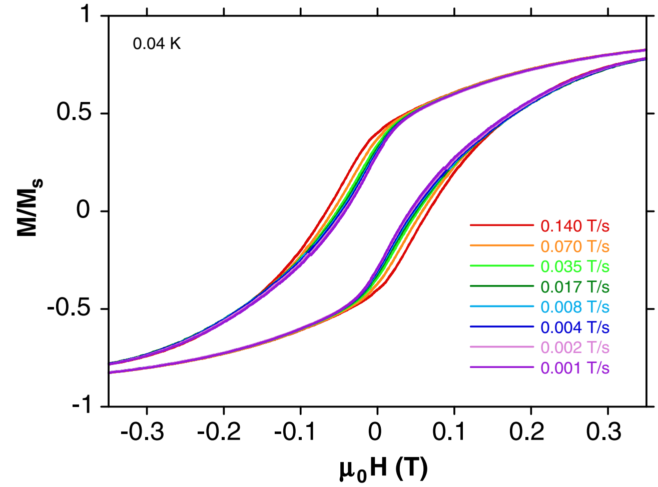


Fig. 6. Magnetization (M) vs field (H) hysteresis loops for a single-crystal of complex **2** · 4MeCN at the indicated field sweep. The magnetization is normalized to its saturation value (M_s).

of Fig. 3. A value of 455 cm^3 mol^{-1} K is consistent with: (i) $S = 59/2$ and $g = 2.01$, (ii) $S = 61/2$ and $g = 1.95$, and (iii) $S = 63/2$ and $g = 1.89$. The AC data thus confirm a high ground state spin of $S = 61/2 \pm 1$.

The $S = 61/2$ ground state and the negative D value suggested that **2** might be an SMM. Indeed, at temperatures <4.0 K, frequency-dependent tails were seen in the out-of-phase (χ_M'') ac susceptibility signals for **2** · 4MeCN whose maxima lie below the operating minimum temperature of our SQUID instrument (1.8 K). Such signals are an indication of the superparamagnetic-like slow relaxation of a SMM, although they do not prove an SMM because intermolecular interactions and phonon bottlenecks can also lead to such signals. The upper limit to the relaxation barrier is $U = (S^2 - 1/4)|D|$ for a half-integer spin, or only 11.2 cm^{-1} (=16.20 K) for **2** · 4MeCN, but the actual (or effective) barrier (U_{eff}) will be significantly less due to magnetization quantum tunneling through the barrier. In order to confirm whether **2** is an SMM, magnetization versus applied dc field data down to 0.04 K were collected on single-crystals using a micro-SQUID apparatus [8]. The resulting magnetization responses at different field sweep rates and a constant temperature of 0.04 K are shown in Fig. 6. The corresponding magnetization responses at different temperatures and a fixed field sweep rate of 0.14 T/s. Hysteresis loops are seen below ~1.0 K whose coercivities increase with increasing sweep rate and with decreasing temperature, as expected for the superparamagnet-like properties of a SMM. This confirms **2** to be an SMM. An Arrhenius plot, constructed from magnetization decay data, gave $U_{\text{eff}} = 6.43$ cm^{-1} $= 9.3$ K and $\tau_0 = 5 \times 10^{-11}$, where τ_0 is the pre-exponential factor.

In summary, we have shown that it really is possible to significantly adjust, or tweak, the spin of an already high-spin molecule by altering the peripheral ligation in a way that does not alter the core structure but nevertheless perturbs the exchange coupling. The spin-tweaking is accomplished in this prototypical case by replacement of a bridging and terminal pair of azides with a chelating/bridging hmp$^-$ group, the chelate ring introducing new types of bridging atoms and also some structural restrictions. As a result, the ground state spin increases from $S = 51/2$ to 61/2.

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Appendix A. Supplementary material

CCDC 617249 and 617248 contain the supplementary crystallographic data for this paper. 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.2006.10.011.

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