

“Spin Tweaking” of a High-Spin Molecule: An Mn₂₅ Single-Molecule Magnet with an $S = 61/2$ Ground State**

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Polynuclear 3d metal complexes are of interest for various reasons, one of which is the possibility that they might exhibit high-spin (S) ground states and easy-axis-type magnetic anisotropy. Such molecules often have a significant energy barrier (vs kT , where k is the Boltzmann constant) to reversal of the magnetization (magnetic moment) vector, and thus at sufficiently low temperatures the molecules function as nanoscale magnetic particles.^[1] In addition, they can display quantum effects such as quantum tunneling of the magnetization (QTM)^[2] 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, QTM through upper regions of the anisotropy barrier means the true or effective barrier (U_{eff}) is less than U .

New high-spin molecules are thus important for the development of new SMMs and also for a fundamental understanding of high-spin species. Large S values can result from ferromagnetic (or ferrimagnetic) spin alignments and/or from competing antiferromagnetic interactions (spin frustration) in certain M_x topologies that prevent (frustrate) perfectly antiparallel spin alignments.^[5] Nevertheless, it is difficult to achieve a rational synthesis of a high-spin species from simple reagents,^[6] 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. Recent examples of such situations include Mn₁₀, Mn₂₅, and Mn₁₉ complexes with $S = 44/2$,^[7] $51/2$,^[8] and $83/2$ ^[9] ground states, respectively, but with minimal anisotropies (i.e. D values).

An alternative potential approach to new high-spin molecules is to structurally perturb a molecule that already has a high spin in some minor way to modify the constituent exchange parameters and possibly alter the ground state (hopefully to a larger rather than smaller value). While this is

often stated as an objective, it has yet to be realized. Note that this is different from the result reported by Perlepes and co-workers^[6] in replacing OH⁻ bridges (that give antiferromagnetic coupling) in Ni and Co clusters with end-on N₃⁻ bridges (that give ferromagnetic coupling); that example represents conversion of a low-spin cluster into one that has a high spin. One of our own early attempts to modify an already high-spin complex was the one- or two-electron reduction of the [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄] family of SMMs with $S = 10$ ground states, but this gave $S = 19/2$ and $S = 10$ ground states, respectively.^[10] Herein, however, we show that it is indeed possible to significantly ($\approx 20\%$) modify the ground-state spin of a complicated, already high-spin molecule without significant core structural change by targeted modification of the peripheral ligation about the magnetic core.

We used the Mn₂₅ SMM [Mn^{II}₆Mn^{III}₁₈Mn^{IV}O₁₈(OH)₂(N₃)₁₂(pdm)₆(pdmH)₆]X₂ (**1**; X = Cl or N₃; pdmH₂ = 2,6-pyridinedimethanol). The X = Cl⁻ salt was prepared originally,^[8] but here we employed the X = N₃⁻ salt (see Experimental Section). The Mn₂₅ cation of **1**^[11] has a barrel-like cage structure involving 12 μ_4 -O²⁻, six μ_3 -O²⁻, and two μ_3 -OH⁻ ions (Figure 1, top). The peripheral ligation is provided by chelating/bridging pdm²⁻/pdmH⁻ ions as well as both terminal and end-on bridging N₃⁻ groups. The core comprises five layers of three types with an ABCBA arrangement (Figure 1, bottom). Layer A comprises 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 a 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 O²⁻, OR⁻, and/or N₃⁻ bridges.

The [Mn₂₅O₁₈(OH)₂(N₃)₁₂(pdm)₆(pdmH)₆]²⁺ cation has an $S = 51/2$ ground state, and we undertook the challenge of tweaking this without core structural change. We decided to target the bridging and terminal azide groups. 1,1- (end-on) azide bridges give ferromagnetic coupling for a wide range of M-N-M angles^[12] and undoubtedly help yield the high $S = 51/2$ ground state of **1**. Thus, their removal ran the risk of drastically decreasing the S value. However, we knew from extensive past experience with pyridine-based alkoxide ligands that the anion of 2-(hydroxymethyl)pyridine (hmp⁻) usually adopts an $\eta^1:\eta^2:\mu_2$ chelating/bridging mode that usually yields ferromagnetic coupling between Mn atoms.^[7,13] We thus targeted replacement of the six pairs of bridging and terminal azide ions by six $\eta^1:\eta^2:\mu_2$ hmp⁻ groups, which proved successful.

The reaction of **1** (X = N₃⁻), Na(hmp), and NaClO₄ in 1:6:6 molar ratio in MeCN/MeOH (5:1 v/v) gave a dark brown solution, from which was subsequently isolated [Mn₂₅O₁₈(OH)(OMe)(hmp)₆(pdm)₆(pdmH)₆](N₃)₂-

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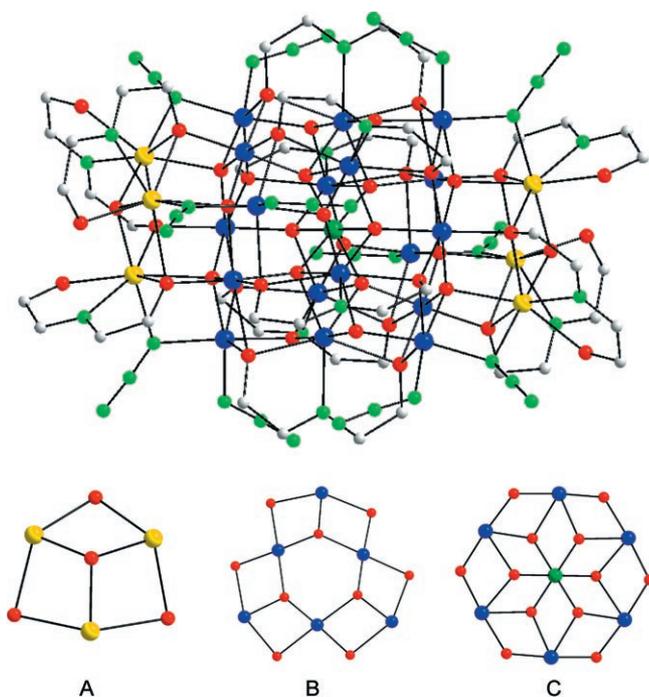


Figure 1. Structure of the cation of **1** (top) and the three types of constituent layers of its core (bottom). Mn^{II} yellow, Mn^{III} blue, Mn^{IV} green (see larger sphere at the center of structure), O red, N green, C gray; H atoms have been omitted for clarity.

(ClO₄)₆·x MeCN·y MeOH (2·x MeCN·y MeOH) in 63 % yield. The crystal structure^[11] shows the core of **2** and **1** to be isostructural. 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,^[14] inspection of metric parameters, and detection of Mn^{III} Jahn–Teller elongation axes. The main difference is that the 12 bound azides of **1** are now replaced by six η¹:η²:μ₂ hmp⁻ ligands in **2** (Figure 2). As a result, all intra- and interlayer bridges, as well as all M₂ pairwise exchange interactions, are now through oxide anions, and there are consequently small metric differences between the cores of **1** and **2**.^[15] There will thus be some changes expected to many of the exchange interactions in the molecule. The ground state of such a large, complicated molecule consisting (undoubtedly) of both ferro- and anti-ferromagnetic interactions will be acutely sensitive to the relative magnitudes of the many exchange interactions, many of which are competing, and it was therefore investigated.

Solid-state direct current (dc) magnetic susceptibility (χ_M) data for dried **2**·4 MeCN were collected in the 5.0–300 K range in an applied field of 1 kG (0.1 T). The product $\chi_M T$ steadily increases from 120.20 cm³ mol⁻¹ K at 300 K to a maximum of 457.42 cm³ mol⁻¹ K at 20 K, before dropping to 401.94 cm³ mol⁻¹ K at 5.0 K (Figure 3). The data measured at 20 K suggest a very large ground-state spin (*S*) value, significantly greater than the *S* = 51/2 spin state of **1**, with the sharp decrease at the lowest temperatures assigned to Zeeman effects, zero-field splitting, and/or weak intermolecular interactions. To determine the ground state, magnetization (*M*) data were collected in the 0.1–1.0 T and 1.8–

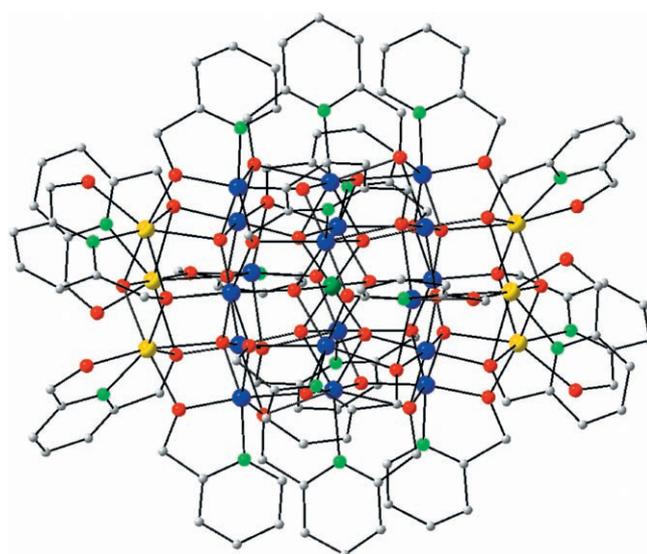


Figure 2. Structure of the cation of **2**. Mn^{II} yellow, Mn^{III} blue, Mn^{IV} green (see larger sphere at the center of structure), O red, N green, C gray; H atoms have been omitted for clarity.

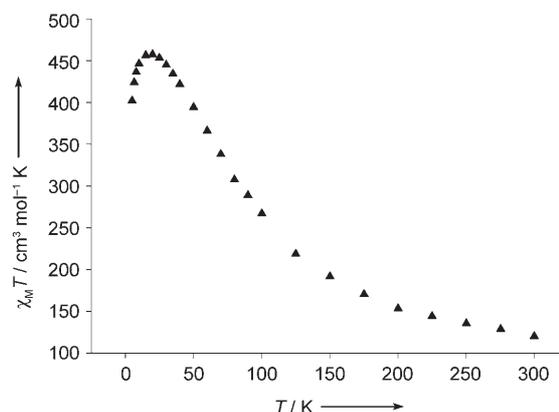


Figure 3. $\chi_M T$ versus *T* plot for complex **2**·4 MeCN in a 1-kG field.

10.0 K ranges and are plotted as *M*/*N*μ_B versus *H*/*T* (*H* = field) in Figure 4. We used only low-field data (≤ 1.0 T), as we previously did for **1**, to avoid problems from low-lying excited states. 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 Figure 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 ± 1. This was confirmed by alternating current (ac) susceptibility experiments in a 3.5 G ac field. The in-phase susceptibility (χ'_M) is shown as $\chi'_M T$ versus *T* in Figure 5, and extrapolation of the $\chi'_M T$ signal to 0 K from above about 8 K (to avoid the effects of intermolecular interactions at lower temperatures) gave 440–470 cm³ mol⁻¹ K, consistent with the dc data (Figure 3). The

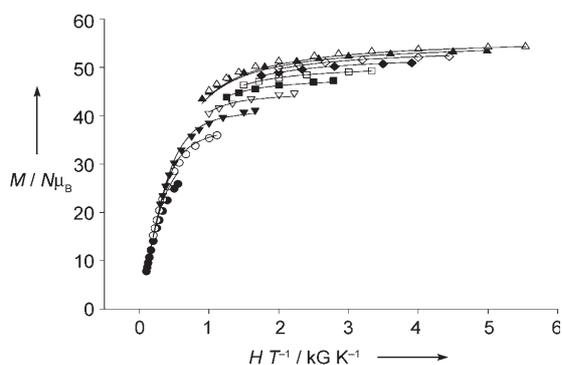


Figure 4. Plot of reduced magnetization ($M/N\mu_B$) versus H/T for 2.4 MeCN in the temperature range 1.8–10 K and in fields of 0.1 T (●), 0.2 T (○), 0.3 T (▼), 0.4 T (▽), 0.5 T (■), 0.6 T (□), 0.7 T (◆), 0.8 T (◇), 0.9 T (▲), and 1.0 T (△). Solid lines show the fit (see text for the fitting parameters).

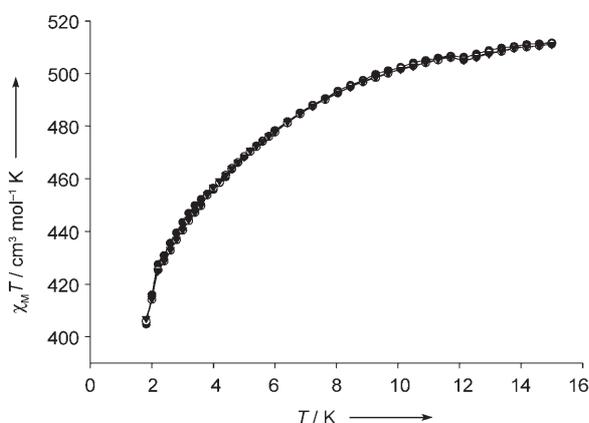


Figure 5. In-phase ac susceptibility ($\chi_M''T$) measurements of complex 2.4 MeCN measured below 15.0 K at frequencies of 1000 Hz (●), 250 Hz (○), and 50 Hz (▼).

value of $\chi_M''T$ of $455 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is consistent with 1) $S = 59/2$ and $g = 2.01$, 2) $S = 61/2$ and $g = 1.95$, and 3) $S = 63/2$ 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. The upper limit to its barrier is $U = (S^2 - 1/4) |D| = 11.2 \text{ cm}^{-1} = 16.1 \text{ K}$, but the true, effective barrier (U_{eff}) will be significantly less as a result of QTM. At temperatures lower than 4.0 K, frequency-dependent tails of out-of-phase (χ_M'') ac susceptibility signals for 2.4 MeCN were observed whose maxima lie below the operating minimum temperature of our SQUID instrument (see Supporting Information). Such signals are an indication of the superparamagnetic-like slow relaxation of a SMM. 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.^[16] Hysteresis loops are seen below about 1.0 K (Figure 6) whose coercivities increase with increasing sweep rate and with decreasing temperature, confirming **2** to be an SMM. The loops do not show the steps characteristic of QTM, as expected for large SMMs, as they are more susceptible to various step-broadening

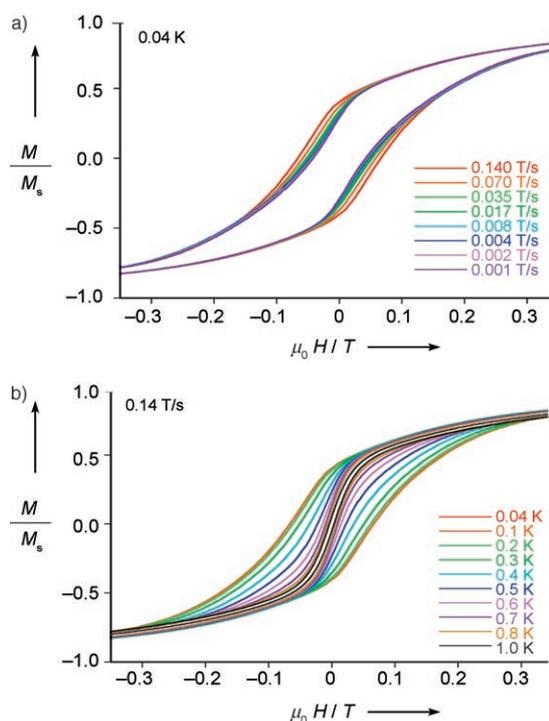


Figure 6. Magnetization (M) versus field (H) hysteresis loops for a single crystal of complex 2.4 MeCN at the indicated field sweep rates (a) and temperatures (b). The magnetization is normalized to its saturation value (M_s).

effects.^[8,17] An Arrhenius plot constructed from magnetization decay data gave $U_{\text{eff}} = 6.43 \text{ cm}^{-1} = 9.3 \text{ K}$ and $\tau_0 = 5 \times 10^{-11}$, where τ_0 is the pre-exponential factor (see Supporting Information).

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. It is thus a proof-of-feasibility for spin tweaking in other high-spin molecules by intelligent variation of the peripheral ligation. The spin was tweaked in this case by targeted replacement of a pair of bridging and terminal azides with a $\eta^1:\eta^2:\mu_2 \text{ hmp}^-$ group, with the restrictive chelate ring introducing structural perturbations as well as new types of bridging atoms. As a result, the ground-state spin increases from $S = 51/2$ to $61/2$, or by about 20%. The precise effect on S could not have been predicted, of course, and it is also difficult to rationalize simply the final $S = 61/2$ value. This is to be expected given the complicated nature of the structure and the many competing antiferromagnetic interactions within its many triangular Mn_3 units, both within individual layers (e.g. layer B) and between separate layers (e.g. layers B and C). The resultant spin of antiferromagnetic Mn_3 triangular units is known to be acutely sensitive to the relative magnitude of the constituent J parameters.^[18] In our previous report of the $S = 51/2$ complex **1** ($X = \text{Cl}^-$), we felt compelled to offer at least some rationalization of the large S value and did so on the basis of layers A, B, and C having $S = 15/2$, 0, and $21/2$, respectively, and with net parallel spin alignment of layers A and C.^[8] However, with hindsight, the implied assumption of

this rationalization that intralayer interactions are significantly stronger than interlayer ones is unjustified, and the resulting spin frustration effects are undoubtedly important to the overall value of S . Finally, note that 1) in one sense, the spin tweaking is a chemical way of perturbing the system analogous to, for example, subjecting a molecular crystal to high pressure, and 2) the conversion of **1** into **2** represents the first time that removal of end-on bridging azide groups has led to an increase in the ground-state S value; usually their addition is sought as a means of raising the value of S .

Experimental Section

Complex **1** was prepared by a slightly modified method to that described previously.^[8] Solid NaN_3 (0.20 g, 3.0 mmol) was added to a stirred solution of pdmH_2 (0.42 g, 3.0 mmol) and Et_3N (0.05 mL, 0.3 mmol) in $\text{MeCN}/\text{H}_2\text{O}$ (25 mL, 10:1 v/v), followed by addition of solid $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.25 g, 1.0 mmol). The resulting dark brown solution was stirred for a further 3 h and filtered, and the filtrate was left undisturbed at ambient temperature. After 5 days, dark brown crystals were collected by filtration, washed with MeCN (2×5 mL), and dried under vacuum (75% yield). Elemental analysis (%) calcd for $\text{C}_{84}\text{H}_{92}\text{Mn}_{25}\text{N}_{54}\text{O}_{44}$ (**1**): C 25.64, H 2.36, N 19.22; found: C 25.77, H 2.32, N 19.34.

2: x MeCN : y MeOH : A dark brown slurry of complex **1** (0.79 g, 0.2 mmol) in MeCN (25 mL) was treated with a solution of $\text{Na}(\text{hmp})$ (0.16 g, 1.2 mmol) and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.17 g, 1.2 mmol) in MeOH (5 mL). The resulting dark brown solution was stirred for a further 1 h and filtered, and the filtrate was left undisturbed at ambient temperature. After 3 days, dark brown prismatic crystals were collected by filtration, washed with MeCN (3×5 mL), and dried under vacuum (63% yield). Analysis of the dried solid confirmed the product to be **2**:4 MeCN . Elemental analysis (%) calcd for $\text{C}_{129}\text{H}_{142}\text{Mn}_{25}\text{N}_{28}\text{O}_{74}\text{Cl}_6$: C 31.92, H 2.95, N 8.08; found: C 31.91, H 2.76, N 7.78. Selected IR data (KBr): $\tilde{\nu} = 3399$ (m), 3068 (m), 2030 (m), 1604 (m), 1438 (m), 1353 (w), 1276 (w), 1228 (m), 1107 (s), 1072 (vs), 776 (m), 633 (vs), 556 (m), 504 (m), 425 cm^{-1} (m).

Safety note: Perchlorate and azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.

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- [11] a) Crystal structure data for **1**:10 MeCN : $\text{C}_{104}\text{H}_{122}\text{Mn}_{25}\text{N}_{64}\text{O}_{44}$, $M_r = 4345.98$, triclinic, space group $P\bar{1}$, $a = 15.9646(12)$, $b = 16.5361(13)$, $c = 17.3483(14)$ Å, $\alpha = 97.895(2)$, $\beta = 101.094(1)$, $\gamma = 117.345(1)^\circ$, $V = 3855.8(5)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.085$ g cm⁻³, $T = 173(2)$ K, 21329 reflections collected, 13437 unique ($R_{\text{int}} = 0.0335$), $R1 = 0.0519$ and $wR2 = 0.1546$, using 13437 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of a half Mn_{25} cluster, one azide anion, and five MeCN molecules of crystallization. The anion and MeCN molecules were disordered and could not be modeled properly, thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Crystal structure data for **2**: x MeCN : y MeOH : $\text{C}_{121}\text{H}_{130}\text{Mn}_{25}\text{N}_{24}\text{O}_{74}\text{Cl}_6$, $M_r = 4690.67$, rhombohedral, space group $R\bar{3}c$, $a = 22.0975(9)$, $c = 69.811(5)$ Å, $V = 29522(3)$ Å³, $Z = 6$, $\rho_{\text{calcd}} = 1.495$ g cm⁻³, $T = 173(2)$ K, 16378 reflections collected, 4080 unique ($R_{\text{int}} = 0.0756$), $R1 = 0.0674$ and $wR2 = 0.1860$, using 4080 reflections with $I > 2\sigma(I)$. The structure consists of Mn_{25} clusters located on $\bar{3}$ symmetry elements. The cluster has a methoxy group on one end of the $\bar{3}$ and a hydroxy group with a perchlorate anion hydrogen-bonded to it on the other end. The solvent molecules were disordered and could not be modeled properly, thus the program SQUEEZE was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. b) CCDC 617249 and 617248 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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- 2.99 (Mn^{III}), and 4.18 (Mn^{IV}); for the oxygen atoms of O²⁻, OH⁻, hmp⁻, pdmH⁻, and pdm²⁻ values of 1.84–2.03 (O²⁻) and 1.16–1.17 (OH⁻, OMe⁻, OR⁻) were obtained; b) W. Liu, H. H. Thorp, *Inorg. Chem.* **1993**, *32*, 4102–4105.
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