

Ferromagnetically-coupled decanuclear, mixed-valence $[\text{Mn}_{10}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}]^{2+}$ [hmpH = 2-(hydroxymethyl)pyridine] clusters with rare T symmetry and an $S = 22$ ground state

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Abstract

The amalgamation of azide (N_3^-) and 2-(hydroxymethyl)pyridine (hmpH) ligands in Mn cluster chemistry has been further investigated. The reactions of hmpH, NaN_3 and Et_3N with $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ or $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in MeCN/MeOH affords $[\text{Mn}_4^{\text{II}}\text{Mn}_6^{\text{III}}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}]\text{X}_2$ [$\text{X} = \text{N}_3^-$ (**1**), ClO_4^- (**2**)]. The Mn_{10} cation has a tetra-face-capped octahedral topology. The central octahedron comprises six Mn^{3+} ions, and the eight faces are bridged by four $\mu_3\text{-N}_3^-$ ions and four $\mu_4\text{-O}^{2-}$ ions. The twelve bridging hmp[−] groups provide the peripheral ligation. This cation is the first example of $\mu_3\text{-1,1,1}$ azido ligands bridging *exclusively* Mn^{3+} ions, presaging a potentially rich new area of Mn^{III} clusters with high spin values. The $[\text{Mn}_{10}(\mu_4\text{-O})_4(\mu_3\text{-N}_3)_4]^{4+}$ core has T_d symmetry, but the complete $[\text{Mn}_4^{\text{II}}\text{Mn}_6^{\text{III}}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}]^{2+}$ cation has rare T symmetry, which is crystallographically imposed. Complexes **1** and **2** are completely ferromagnetically coupled, and have a resulting $S = 22$ ground state, one of the highest yet reported.

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The study of molecules possessing unusually large spin (S) values in their ground state is an area of intense current research [1]. These efforts are driven by a number of considerations, including the desire to elucidate the various factors responsible for yielding high-spin molecules. These include the topological arrangement of the paramagnetic ions, the nature (ferromagnetic or antiferromagnetic) of the inter-ion exchange interactions, and the presence of spin frustration effects. In addition, it has recently become apparent that a fairly large ground state spin S is one of the necessary requirements for molecules to exhibit the phenomenon of single-molecule magnetism [2]. Another

requirement is a significant magnetoanisotropy, as reflected in the zero-field splitting (ZFS) parameter D , which also needs to be negative. One area in which high-spin molecules are frequently encountered is manganese cluster chemistry [3], and the significant anisotropy afforded by octahedral, Jahn–Teller distorted Mn^{III} ions also makes this metal the main source of SMMs to date. Spin values of $S \leq 83/2$ have been observed; for calibration, the largest S values observed to date in a molecular species is $S = 83/2$ for a $\text{Mn}_7^{\text{II}}\text{Mn}_{12}^{\text{III}}$ compound [1h], and $S = 51/2$ for a $\text{Mn}_6^{\text{II}}\text{Mn}_{18}^{\text{III}}\text{Mn}^{\text{IV}}$ complex [1e] and a cyano-bridged $\text{Mn}_9^{\text{II}}\text{Mo}_6^{\text{V}}$ system [1f].

The development of synthetic procedures to new examples of high-spin molecules is thus of continuing interest. However, it is difficult to predict what type of topology

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and structure will lead to a high-spin cluster and even more difficult to then synthesize such a species [4]. Moreover, it is also important in this area of chemistry to not only make new examples of high-spin molecules and single-molecule magnets (SMMs), but also to build up families of related compounds so that structure–property relations can be investigated. Towards this end, two successful but opposite strategies have been employed. The first is the use of rigid bridging ligands that impose structural restrictions on the geometry of the resultant cluster [5], and the second is the use of flexible ligands that impose little or no restrictions [6].

In the majority of polynuclear metal complexes, exchange interactions are mainly propagated by bridging OH^- , OR^- , O^{2-} , or RCO_2^- groups (or a combination of these), ligands which usually lead to antiferromagnetic coupling. One approach for increasing the ground state S is the replacement of some or all of these bridges with groups that promote ferromagnetic coupling. One of the best examples of the latter is the azide (N_3^-) group bridging metal ions in the 1,1-fashion (end-on); in this case the exchange coupling is ferromagnetic for a wide range of M–N–M angles [7]. We also have a continuing interest in the usefulness of flexible pyridine-based alkoxide ligands (Fig. 1) in Mn cluster chemistry, and have noticed that the anion of 2-(hydroxymethyl)pyridine (hmp^-) is a versatile N,O-chelating and bridging ligand whose alkoxide arm often supports ferromagnetic coupling between the metal atoms it bridges [8].

In this paper, we describe two mixed-valence Mn_{10} clusters of formula $[\text{Mn}_4^{\text{II}}\text{Mn}_6^{\text{III}}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}](\text{X})_2$ [$\text{X} = \text{N}_3^-$ (**1**), ClO_4^- (**2**)] obtained by using a combination of N_3^- and hmp^- groups in certain Mn reactions. They possess very aesthetically pleasing structures of high (T) symmetry, and are completely ferromagnetically coupled with a resulting $S = 22$ ground state, one of the highest yet reported [9]. In addition, the Mn_{10} cation is the first

example of μ_3 -1,1,1 azido ligands bridging *exclusively* Mn^{3+} ions, and thus presages a potentially rich new area of Mn^{III} clusters with high spin values.

A reaction mixture of $\text{Mn}(\text{NO}_3)_2$, hmpH , Et_3N and NaN_3 in a 1:1:1:1 ratio in MeCN/MeOH (20:1, v/v) gave a dark brown solution from which was subsequently isolated dark-brown hexagonal crystals of $[\text{Mn}_{10}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}](\text{N}_3)_2$ (**1**) in 20% yield. The use instead of $\text{Mn}(\text{ClO}_4)_2$ gave the isostructural $[\text{Mn}_{10}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}](\text{ClO}_4)_2 \cdot \text{MeCN}$ (**2** · MeCN) in a much higher yield of 75%. The latter reaction but using only MeOH as reaction solvent gave known $[\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}(\text{N}_3)_2(\text{hmp})_6]_n(\text{ClO}_4)_{2n}$ (**3**), which is a one-dimensional chain [8c].

The cation $[\text{Mn}_{10}\text{O}_4(\text{N}_3)_4(\text{hmp})_{12}]^{2+}$ (Fig. 2) consists of ten Mn ions with a tetra-face-capped octahedral topology (Fig. 3). The central octahedron comprises six Mn^{3+} ions, and the eight faces are bridged by four $\mu_3\text{-N}_3^-$ ions and four $\mu_4\text{-O}^{2-}$ ions, with the latter also bridging to four external Mn^{2+} ions that thus cap four non-adjacent faces of the octahedron (Fig. 1). The $\mu_3\text{-N}_3^-$ ions bind in an $\eta^1:\eta^1:\eta^1$ (end-on) fashion. The $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ and O oxidation states were assigned using a combination of charge balance, bond length considerations, bond valence sum (BVS) calculations [10], and the presence of the JT distortions expected for octahedral Mn^{3+} . All Mn^{3+} ions (Mn2 and its symmetry related partners) are six-coordinate with near-octahedral geometry and thus display a Jahn–Teller (JT) distortion, which takes the form of an axial elongation of the two *trans* Mn– N_{azide} bonds (2.412(3) Å). The four Mn^{2+} ions (Mn1 and its symmetry related partners) are seven-coordinate with distorted face-capped octahedral geometry, the capping atom being the oxide atom O1 ($\text{Mn}^{2+}\text{–O}^{2-} = 2.304(4)$ Å). The peripheral ligation about the $[\text{Mn}_{10}(\mu_4\text{-O})_4(\mu_3\text{-N}_3)_4]^{14+}$ core is provided by the twelve hmp^- groups. Three of the latter bind terminally through their N atom to each of the exterior Mn^{2+} ions, with their alkoxide arms bridging this Mn^{2+} ion to a Mn^{3+} ion (Mn2)

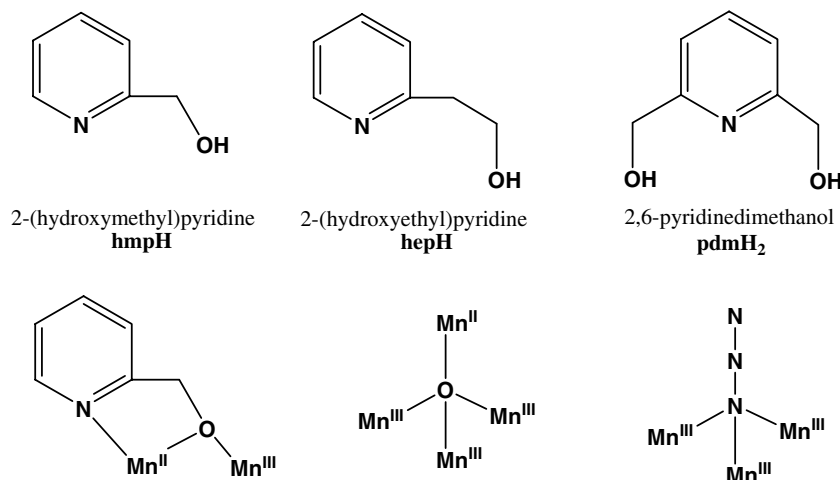


Fig. 1. The pyridyl-alcohol ligands discussed in the text (top), and the crystallographically established coordination modes of the hmp^- , oxo and azido ligands present in complexes **1** and **2** (bottom).

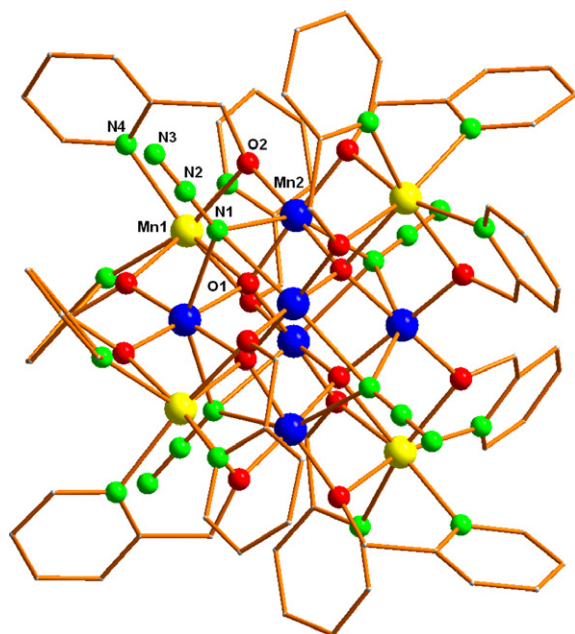


Fig. 2. The structure of the cation of **2**. Color code: Mn^{II} yellow, Mn^{III} blue, O red, N green, C gray. H atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Mn1–O1 2.304(2), Mn1–O2 2.242(3), Mn1–N4 2.288(3), Mn2–O1 1.908(2), Mn2–O2 1.889(3), Mn2–N1 2.412(3), Mn1···Mn1 6.534(1), Mn1···Mn2 3.267(1), Mn2···Mn2 3.239(1), Mn1–O1–Mn2 101.4(1), Mn1–O2–Mn2 104.3(1), Mn2–O1–Mn2 116.2(1), Mn2–N1–Mn2 84.4(9). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

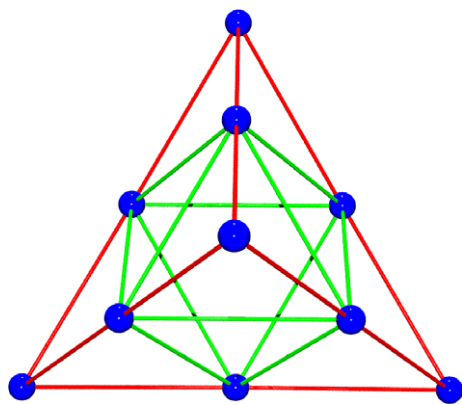


Fig. 3. The Mn₁₀ topology, emphasizing the tetra-face-capped octahedral description. Red and green lines indicate the Mn²⁺···Mn³⁺ and Mn³⁺···Mn³⁺ vectors, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 1). There are only weak intermolecular interactions, which involve the hmp phenyl groups.

Complexes **1** and **2** join only a handful of previous mixed-valent Mn₁₀ clusters [11], and are the first at the 4Mn²⁺, 6Mn³⁺ level. The [Mn₁₀(μ₄-O)₄(μ₃-N₃)₄]¹⁴⁺ core has *T_d* symmetry, but inclusion of the hmp groups removes the σ_d planes and *S*₄ axes, and the complete [Mn₄^{II}Mn₆^{III}O₄(N₃)₄(hmp)₁₂]²⁺ cation consequently has rare

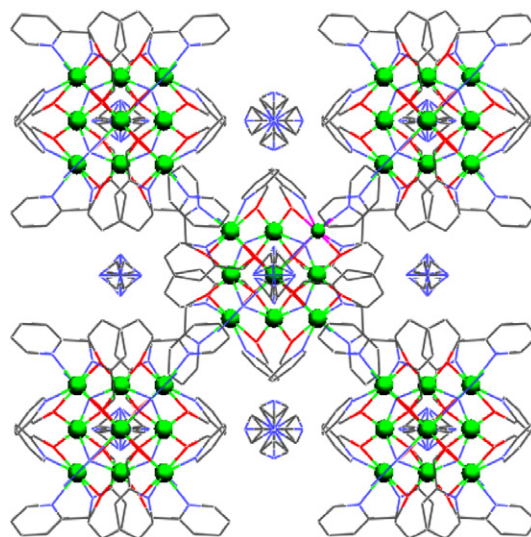


Fig. 4. Packing diagram of **1** along the *a*-axis. N₃[−] counter ions are located in the middle of each neighboring Mn₁₀ molecules.

T point group symmetry, which is crystallographically imposed; point group *T* is the rotational sub-group of *T_d*. This aesthetically pleasing symmetry extends to the packing of the molecules in the crystal, as shown in Fig. 4.

The magnetic behavior of the two complexes is similar. As a result of the high-yield of complex **2** (compared to that of **1**), magnetic data are presented only for the former cluster. Solid-state DC magnetic susceptibility (χ_M) data for complex **2** · MeCN were collected in the temperature range 5.0–300 K in an applied field of 1 kG (0.1 T). The $\chi_M T$ value steadily increases from 53.78 cm³ mol^{−1} K at 300 K to a maximum of 231.56 cm³ mol^{−1} K at 10 K, before dropping to 220.23 cm³ mol^{−1} K at 5.0 K (Fig. 5).

The spin-only (*g* = 2) value for a non-interacting [Mn₄^{II}Mn₆^{III}] unit is 35.5 cm³ mol^{−1} K. This indicates ferromagnetic exchange interactions within **2** and the 10 K data strongly suggest a very large ground-state spin (*S*) value, with the sharp decrease at the lowest temperatures assigned to Zeeman effects, zero-field splitting and/or weak intermo-

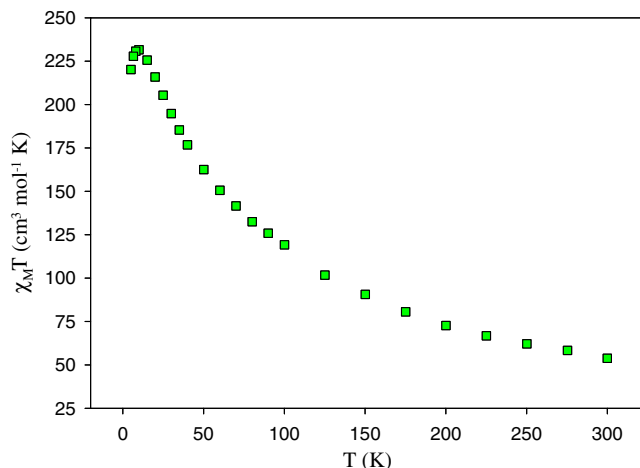


Fig. 5. $\chi_M T$ vs. *T* plot for complex **2** · MeCN in a 1 kG field.

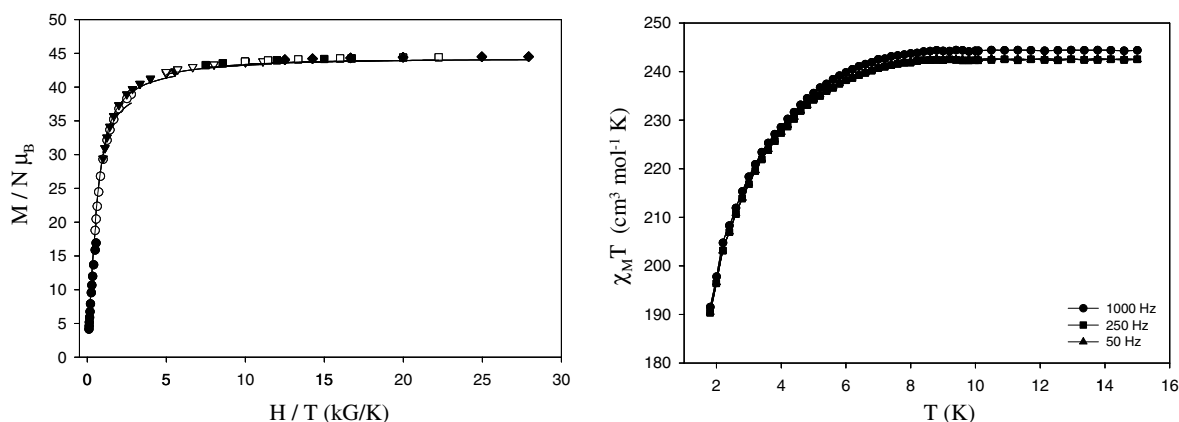


Fig. 6. Plot of reduced magnetization ($M/N\mu_B$) vs. H/T for $2 \cdot \text{MeCN}$ in the temperature range 1.8–10 K and in fields of 0.1 T (●), 0.5 T (○), 1.0 T (▼), 2.0 T (▽), 3.0 T (■), 4.0 T (□), 5.0 T (◆). The solid lines are fits of the data (left). In-phase ac susceptibility ($\chi_M' T$) measurements of complex $2 \cdot \text{MeCN}$ measured below 15.0 K at the indicated frequencies (right).

lecular interactions. The 10 K value is consistent with an $S = 22$ ground state, the maximum possible, and a g value slightly less than 2.0, as expected for a $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ complex; the spin-only ($g = 2$) value for an $S = 22$ state is $253 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$.

In order to confirm the ground state of $2 \cdot \text{MeCN}$, magnetization (M) data were collected in the 0.1–5 T and 1.8–10.0 K ranges, and these are plotted as $M/N\mu_B$ versus H/T in Fig. 6. The various isofield lines are virtually superimposed, indicating essentially no zero-field splitting (ZFS) within the ground state, and the saturation value of $M/N\mu_B \approx 44$ is consistent with $S = 22$. 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. 4) gave $S = 22$, $g = 2.00(1)$ and $D = -0.011(1) \text{ cm}^{-1}$, confirming a very high-spin ground state with little or no magnetic anisotropy. The $S = 22$ ground state was further supported by alternating current (ac) susceptibility experiments, in which a weak field of 3.5 G oscillating at a particular frequency (ν) was applied to the sample. 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 $2 \cdot \text{MeCN}$ is shown as $\chi_M' T$ versus T in Fig. 6, and $\chi_M' T$ can be seen to be temperature-independent at $\sim 244 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ from 15 K down to ~ 8 K, and this temperature-independent value is consistent with $S = 22$ and $g \sim 1.96$, in satisfying agreement with the dc magnetization fits. The temperature-independent $\chi_M' T$ also indicates no population of excited states in this temperature range. At lower temperatures, $\chi_M' T$ decreases slightly, which we assign to weak intermolecular interactions, both dipolar and superexchange in nature.

There is no out-of-phase (χ_M'') ac susceptibility signal down to 1.8 K, which indicates an insignificant barrier (versus kT) to magnetization relaxation. To explore whether slow relaxation might become apparent at even lower tem-

peratures, magnetization vs dc field scans were performed on a single crystal of $2 \cdot \text{MeCN}$ down to 0.04 K. No hysteresis was observed. The combined results indicate an isotropic crystal and fast magnetization relaxation even at 0.04 K, which are consistent with $D \sim 0$.

In summary, the combination of azide and hmp^- ligands in Mn cluster chemistry has yielded an unusual cation that has both a very high $S = 22$ ground state value and high (T) symmetry. Such a high S value is extremely rare, very similar in magnitude to the $S = 23$ for an Fe_{14} cluster, the largest S in Fe chemistry [1g].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2006.09.096](https://doi.org/10.1016/j.poly.2006.09.096).

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