



1-D coordination polymers consisting of a high-spin Mn₁₇ octahedral unit

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ABSTRACT

The reaction of [Mn(O₂CMe)₂] · 4H₂O with pdH₂ (1,3-propanediol) or mpdH₂ (2-methyl-1,3-propanediol) in the presence of NaN₃ in MeCN/py (py = pyridine) results in the formation of two new one-dimensional coordination polymers composed of a [Mn^{II}₆Mn^{III}₁₁(μ₄-O)₈(μ₃-N₃)₄]²⁵⁺ octahedral unit. The peripheral ligation is completed by pd²⁻ (or mpd²⁻), acetate, pyridine and μ-1,3-N₃⁻ ligands. The latter bridges each Mn₁₇ unit to its neighboring one, resulting in the formation of the two 1-D coordination polymers. Variable-temperature dc magnetic susceptibility studies indicate the existence of predominantly ferromagnetic interactions and a resulting giant ground state spin within the Mn₁₇ units and intermolecular antiferromagnetic exchange interactions between the neighboring Mn₁₇ units that result in diamagnetic ground spin states for both polymeric compounds.

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Polynuclear Mn clusters continue to attract great attention, mainly due to their aesthetically-pleasing structures and the often unusual and sometimes novel magnetic properties. Such molecules may exhibit high and sometimes abnormally high ground state spin values currently up to $S = 83/2$ [1], and single-molecule magnetism (SMM) behavior [2]. High-spin molecules are important for a number of reasons including: (i) the development of new SMMs since a fairly large ground spin state is one of the necessary (but not sufficient) requirements for molecules to be able to exhibit SMM behavior, (ii) their use as building-blocks for the construction of new single-chain magnets (SCMs) and also of 2- and 3-D coordination polymers with interesting magnetic properties, and (iii) the purely fundamental desire to understand exactly how the sign and relative magnitudes of the constituent exchange interactions yield the high S value. Although several metal clusters with abnormally high-spin ground states are currently known, including the Mn₁₉ family of clusters with $S = 83/2$ [1] and $73/2$ [3] and the Mn₂₅ family of 'barrel'-like clusters with $S = 51/2$ [4] and $61/2$ [5], it is still very difficult to predict what type of topology and structure will lead to a high-spin cluster, and even more difficult to achieve a rational synthesis of such a species.

For all those reasons, there is a continuing interest in the development of synthetic procedures to new high-spin molecules from simple reagents [6]. One of the most successful approaches em-

ployed to date for the synthesis of new high-spin molecules involves the use of bridging ligands that result in ferromagnetic exchange interactions. One of the best of these is the azide (N₃⁻) group when it bridges metal ions in the 1,1 (end-on) fashion, in which case the exchange coupling is ferromagnetic for a wide range of M–N–M angles [7]. Recently, we have been investigating the use of 1,3-propanediol (pdH₂) and its derivatives in Mn carboxylate chemistry and we have been able to isolate new polynuclear clusters, some of which have a relatively large spin ground state [8].

Herein, we report two new 1-D coordination polymers, [Mn₁₇(μ₄-O)₈(N₃)₅(O₂CMe)₄(pd)₁₀(py)₆]_∞ (**1**)_∞ and [Mn₁₇(μ₄-O)₈(N₃)₅(O₂CMe)₄(mpd)₁₀(py)₈]_∞ (**2**)_∞, which are the initial products of the use of both pdH₂ (or mpdH₂) and N₃⁻ in reactions with simple Mn^{II} carboxylate salts. These two compounds contain an aesthetically-pleasing [Mn^{II}₆Mn^{III}₁₁(μ₄-O)₈(μ₃-N₃)₄]²⁵⁺ octahedral unit with a very large ground state spin, the exact value of which was impossible to determine due to the covalent linkage of neighboring Mn₁₇ units that introduced intermolecular magnetic interactions.

The reaction of [Mn(O₂CMe)₂] · 4H₂O, pdH₂ and NaN₃ in a 1:5:1 ratio in MeCN/py (10:2, v/v) gave a yellowish-brown solution from which was subsequently isolated a dark brown crystalline solid of {[Mn₁₇(μ₄-O)₈(N₃)₅(O₂CMe)₄(pd)₁₀(py)₆] · 2H₂O}_∞ (**1** · 2H₂O)_∞¹ in 30% yield (single crystals could be obtained as

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¹ Elemental analysis (%): Anal. Calc. for C₆₈H₁₀₆O₃₈N₂₁Mn₁₇ (1 · 2H₂O): C, 29.60; H, 3.87; N, 10.66. Found: C 29.74, H 3.71, N 10.53%. Anal. Calc. for C₈₈H₁₃₆O₃₈N₂₃Mn₁₇ (2 · 2H₂O): C, 34.56; H, 4.48; N, 10.53. Found: C, 34.76; H, 4.32; N, 10.69%.

($1 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$). When the same reaction was repeated with mpdH₂ instead of pdH₂, {[Mn₁₇(μ₄-O)₈(N₃)₅(O₂CMe)₄(mpd)₁₀(py)₈]} $_{\infty}$ ($2 \cdot 2\text{H}_2\text{O}$) $_{\infty}$ ¹ was isolated in 35% yield (single crystals could be obtained as ($2 \cdot 2.2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$).

The crystal structures of ($1 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$ ² (Fig. 1a) and ($2 \cdot 2.2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$ ³ both having crystallized in the triclinic space group *P* $\bar{1}$, consist of a [Mn₁₇(μ₄-O)₈(μ₃-N₃)₄(O₂CMe)₂(L)₁₀]³⁺ (L = pd²⁻ (**1**); mpd²⁻ (**2**)) unit with a flattened octahedral topology. Bond-valence sum calculations [9], charge considerations, and inspection of metric parameters revealed a mixed-valent complex containing six Mn^{II} and eleven Mn^{III} ions. The 15 Mn ions of the core (Fig. 1b) are disposed in three nearly planar rectangles stacked one above the other, and the remaining two Mn ions occupy the top and bottom capping positions. The central plane consists of seven Mn ions, four at the vertices, two on opposite edges, and the seventh near its center, whereas each of the other two planes contains four Mn ions all of which lie on the edges. All the Mn^{II} ions are located at the vertices of the octahedron whereas the Mn^{III} ions are placed on the edges and near the center of the octahedron. The Mn ions of the core are held together by eight μ₄-O²⁻ and four μ₃-1,1,1-N₃⁻ ligands. The structures also contain ten bridging pd²⁻ (or mpd²⁻), two bridging and two chelating acetate ligands and one μ-1,3-N₃⁻ group. The peripheral ligation of compounds **1** and **2** is completed by six and eight terminal pyridine groups, respectively. The μ-1,3-N₃⁻ ligands bridge Mn7 ion of the Mn₁₇ unit to its symmetry-related Mn ion of the neighboring Mn₁₇ unit resulting in the formation of the 1-D coordination polymer (Fig. 2). The shortest Mn...Mn separation between different Mn₁₇ units is ~6.24 Å in ($1 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$ and slightly longer (6.421 Å) in ($2 \cdot 2.2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$. The chains run parallel in the crystal, and although there are H₂O and MeCN molecules of crystallization there are no significant interchain interactions.

Variable-temperature, solid state magnetic susceptibility measurements were performed on powdered polycrystalline samples of ($1 \cdot 2\text{H}_2\text{O}$) $_{\infty}$ and ($2 \cdot 2\text{H}_2\text{O}$) $_{\infty}$ in a 1 kG (0.1 T) field in the 5.0–300 K range. The obtained data for both compounds are shown as χ_MT versus *T* plots in Fig. 3. The χ_MT for ($1 \cdot 2\text{H}_2\text{O}$) $_{\infty}$ and ($2 \cdot 2\text{H}_2\text{O}$) $_{\infty}$ increases from 82.5 and 88.4 cm³ mol⁻¹ K at 300 K to a maximum of 375.4 and 428.1 cm³ mol⁻¹ K at 40.0 and 35 K, respectively, before dropping rapidly to 67.9 and 156.4 cm³ mol⁻¹ K at 5.00 K. The 300 K χ_MT values are significantly larger than the value expected if the constituent Mn^{II}Mn^{III} atoms were non-interacting (59.25 cm³ mol⁻¹ K for *g* = 2) suggesting the presence of predominant ferromagnetic exchange interactions within the Mn₁₇ units. The maximum χ_MT values indicate a very large ground state spin [for example, the χ_MT value of 428.1 cm³ mol⁻¹ K for ($2 \cdot 2\text{H}_2\text{O}$) $_{\infty}$ is consistent with an *S* = 29 spin ground state, for which the spin-only (*g* = 2) value is 435.0 cm³ mol⁻¹ K].

The low temperature steep decrease is undoubtedly due to intermolecular antiferromagnetic exchange interactions mediated by the end-to-end N₃⁻ ligands, resulting in a diamagnetic ground state for both polymeric species. This was confirmed by the in-phase ac susceptibility (χ_M^{ac}), plotted as χ_M^{ac} versus *T* in Fig. 4, for the two polymers, which are clearly heading for zero at 0 K. This shows that the steep decrease of χ_MT in Fig. 3 is not due to an arte-

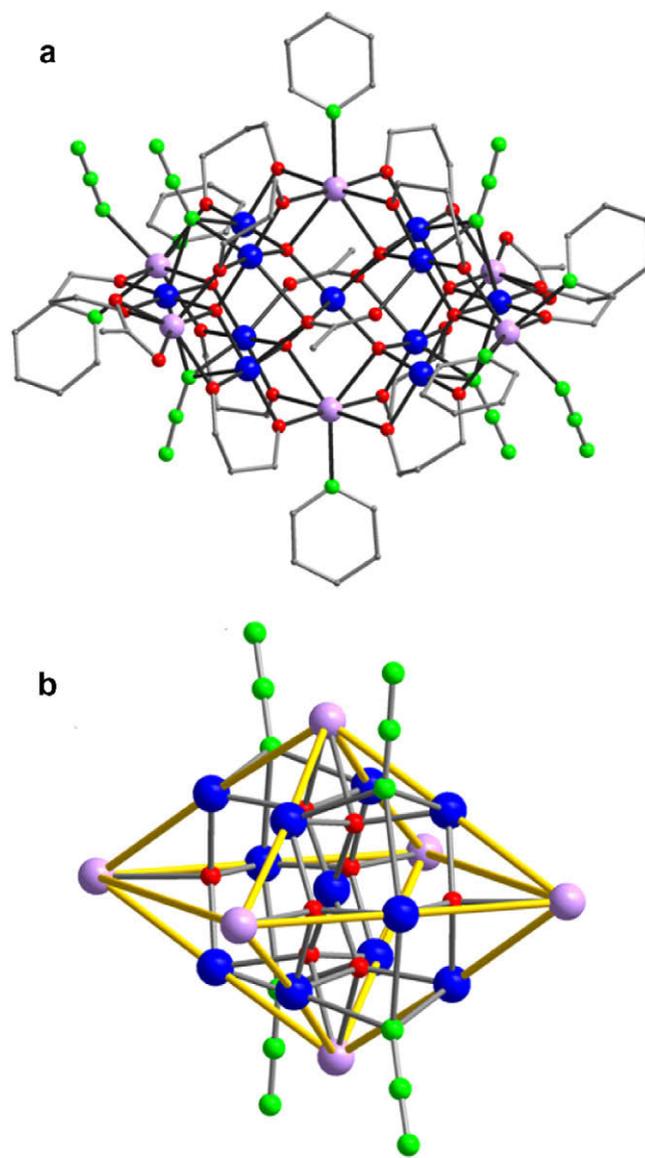


Fig. 1. (a) The molecular structure of **1**. (b) The [Mn^{III}₁₁Mn^{II}₆(μ₄-O)₈(μ₃-N₃)₄]²⁵⁺ octahedral core of **1** and **2**. Color code: Mn^{II}, blue; Mn^{III}, purple; O, red; N, green; C, grey. Hydrogen atoms have been omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fact of the applied dc field but indeed due to intermolecular interactions within the 1-D polymers.

In summary, the use of N₃⁻ ligands in Mn-propanediol chemistry has resulted in the isolation of two new one-dimensional coordination polymers based on a Mn₁₇ repeating unit. Each Mn₁₇ unit has an aesthetically-pleasing structure, in which the manganese ions have an octahedral topology. Furthermore, the repeating unit seems to have a giant ground spin state, but the connection of the clusters through the μ-1,3-N₃⁻ bridges results in antiferromagnetic intermolecular interactions between the neighboring Mn₁₇ units and thus each polymer has an effective *S* = 0 spin ground state. The high-spin ground state for each Mn₁₇ cluster is consistent with the presence of μ₃-1,1,1-N₃⁻ ligands, which are known to mediate ferromagnetic interactions [7]. Substitution of the μ-1,3-N₃⁻ ions with terminal ligands could lead to magnetically discrete Mn₁₇ aggregates with interesting magnetic properties, instead of the present one-dimensional polymers, and such studies are in progress. Finally, the existence of a number of labile terminal ligands

² Crystallographic data for ($1 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$: C₇₂H₁₁₂N₂₃O₃₈Mn₁₇, *M_r* = 2841.80 g mol⁻¹, triclinic, space group *P* $\bar{1}$, *a* = 14.051(2) Å, *b* = 14.700(2) Å, *c* = 15.200(2) Å, α = 81.60(1)°, β = 66.66(2)°, γ = 78.31(1)°, *V* = 2815.2(6) Å³, *T* = 100(2) K, *Z* = 1, ρ_{calc} = 1.676 g cm⁻³, 43934 reflections collected, 12176 unique (*R*_{int} = 0.0424), *R*₁ = 0.0379, *wR*₂ = 0.0938, using 6131 reflections with *I* > 2σ(*I*).

³ Crystallographic data for ($2 \cdot 2.2\text{H}_2\text{O} \cdot 2\text{MeCN}$) $_{\infty}$: C₉₂H_{142.4}N₂₅O_{38.2}Mn₁₇, *M_r* = 3143.85 g mol⁻¹, triclinic, space group *P* $\bar{1}$, *a* = 14.8717(7) Å, *b* = 16.3561(6) Å, *c* = 16.9541(9) Å, α = 65.231(4)°, β = 65.975(5)°, γ = 67.563(4)°, *V* = 3307.5(3) Å³, *T* = 100(2) K, *Z* = 1, ρ_{calc} = 1.578 g cm⁻³, 43279 reflections collected, 11518 unique (*R*_{int} = 0.0323), *R*₁ = 0.0492, *wR*₂ = 0.1442, using 6772 reflections with *I* > 2σ(*I*).

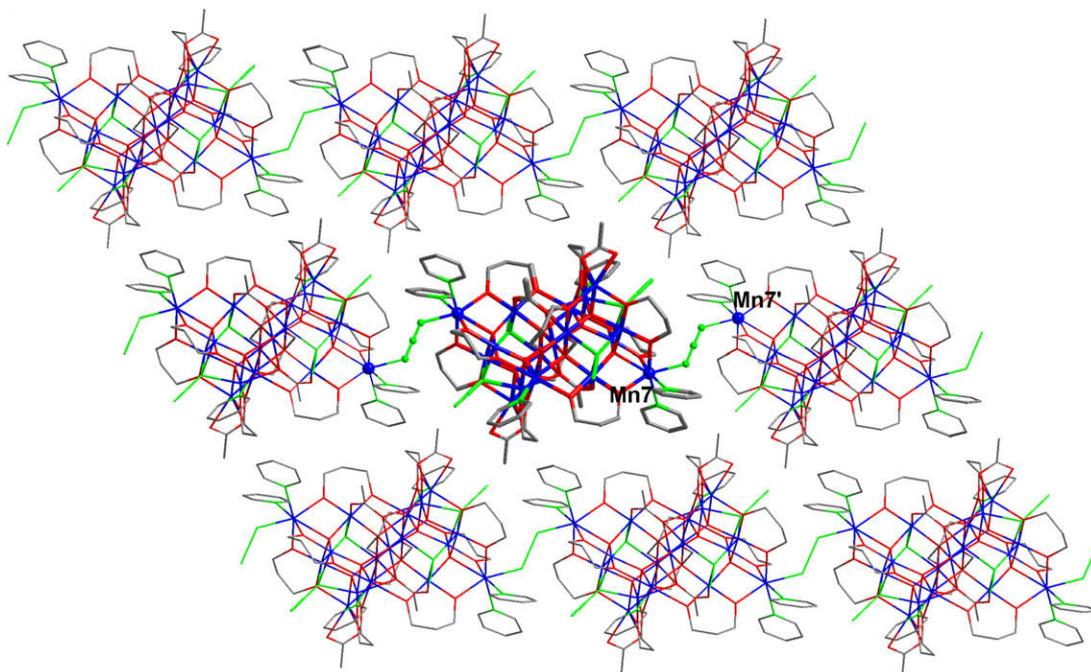


Fig. 2. Wire-frame representation of small sections of $(1)_{\infty}$ emphasizing the connection of the Mn_{17} units to form the overall 1-D polymeric networks. Color code: Mn, blue; O, red; N, green; C, grey. Hydrogen atoms have been omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

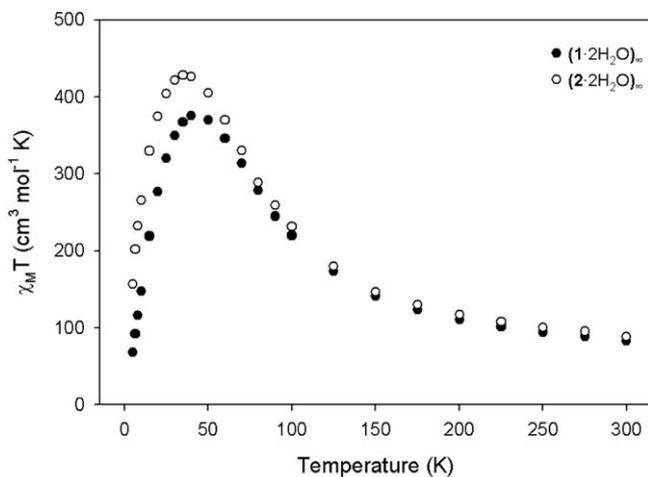


Fig. 3. Plots of $\chi_M T$ vs. T for $(1 \cdot 2H_2O)_{\infty}$ and $(2 \cdot 2H_2O)_{\infty}$.

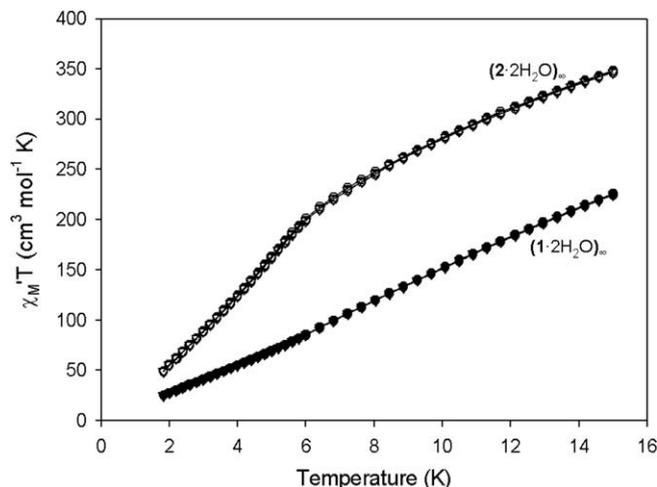


Fig. 4. Temperature-dependence of the in-phase (χ'_M) ac magnetic susceptibility of $(1 \cdot 2H_2O)_{\infty}$ and $(2 \cdot 2H_2O)_{\infty}$ at frequencies 50, 250, and 1000 Hz.

in each Mn_{17} units, offers a variety of possibilities for using them as building-blocks for the construction of multidimensional coordination polymers with interesting magnetic and/or structural properties.

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Appendix A. Supplementary data

CCDC 699771 and 708857 contain the supplementary crystallographic data for this article. 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.2008.12.023.

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