



High-spin molecules: A mixed-valence Mn₆ octahedron with an *S* = 11 ground state

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ABSTRACT

The employment of 1,1,1-tris(hydroxymethyl)ethane ligand in higher oxidation state Mn cluster chemistry has yielded a new hexanuclear, mixed-valence (II,III,IV) compound with a rare [Mn₆(μ₆-O)]¹⁸⁺ octahedral core. The Mn₆ molecule is completely ferromagnetically coupled and possesses an *S* = 11 ground state, the maximum for a Mn^{II}, 2Mn^{III}, 3Mn^{IV} species.

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The search for large clusters of paramagnetic transition metal ions has been greatly stimulated by the discovery of single-molecule magnetism [1]. This is the superparamagnetic-like behaviour of molecular species that combines a large spin ground state, *S*, with a relatively large magnetoanisotropy of the easy-axis-type (as reflected in a negative zero-field splitting parameter, *D*) [2]. This results in a significant barrier (*U*) to magnetization reversal, whose upper limit is given by *S*²|*D*| or (*S*² – 1/4)|*D*| for integer and half-integer spin, respectively, and the observation of both hysteresis in magnetization vs DC magnetic field sweeps, and frequency-dependent out-of-phase AC magnetic susceptibility signals. SMMs thus represent a molecular or “bottom-up” approach to nanoscale magnetism.

There are now many structural types of molecular complexes that display such SMM behaviour, and the majority of these are Mn species, since coordination clusters of this metal often display large ground state spin (*S*) values, as well as negative *D* values resulting from the presence of Jahn-Teller distorted Mn^{III} atoms [3]. This rationalizes the fact that most successful searches for new high-spin molecules and SMMs have involved Mn^{III} chemistry, partially or exclusively. In fact, only a relatively few SMMs have contained exclusively Mn^{III} [4]; most Mn SMMs have instead been valence-localized (class II) mixed-valence clusters containing Mn^{III}, and have included Mn^{II}/Mn^{III}, Mn^{III}/Mn^{IV} and Mn^{II}/Mn^{III}/Mn^{IV} oxidation state mixtures [1a,3]. For the latter type of clusters spanning three Mn oxidation states, there are only a few examples reported to date [5]. However, the present work deals with a new example of such a Mn^{II/III/IV} molecular species, which has an interesting Mn₆ core topology and a high-spin ground state.

The reaction of MnCl₂ · 4H₂O, KMnO₄, and 1,1,1-tris(hydroxymethyl)ethane (thmeH₃) in a 3:1:3 molar ratio in MeCN gave a dark brown suspension upon stirring for 3 h. The dark brown solid was isolated by filtration, washed with cold MeCN (1 × 3 mL) and dried in air for 24 h. Recrystallization from a CH₂Cl₂/Et₂O/*n*-hexane layering gave after five days dark brown crystals of [Mn₆OCl₃(thme)₅] · 3CH₂Cl₂ (**1** · 3CH₂Cl₂) in 65% yield.¹

The structure of **1**² is shown in Fig. 1 and contains a core comprising a Mn₆ octahedron with a central μ₆-O²⁻ ion, atom O(1). Charge considerations and the metric parameters indicate a Mn^{II}-Mn^{III}/Mn^{IV} mixed-valence situation. This was confirmed by BVS calculations [6], which clearly identified Mn(4), Mn(5) and Mn(6) as Mn^{IV} atoms, and Mn(3) as Mn^{III}. The BVS for Mn(1) and Mn(2) (2.35 and 2.64, respectively; total 4.99, average 2.50) are intermediate between those expected for Mn^{II} and Mn^{III}, and we assign this to a static disorder of Mn^{II} and Mn^{III} between these two positions (vide infra). The complex is thus at the Mn^{II}Mn^{III}Mn^{IV} oxidation level. The twelve edges of the Mn₆ octahedron are each monoatomically bridged by a thme³⁻ alkoxide arm to give an overall [Mn₆(μ₆-O)(μ-OR)₁₂]⁶⁺ unit (Fig. 2). The thme³⁻ groups are each bridging three Mn atoms, but with different binding modes as shown in Fig. 3. The peripheral ligation is completed by three terminal Cl⁻ ions bound to the Mn^{II}/Mn^{III} atoms Mn(1)–Mn(3). The overall molecule has C_{3v} symmetry, if we ignore the different oxidation states of

¹ Elemental Anal. Calc. for C₂₅H₄₅Mn₆Cl₃O₁₆ (**1**): C, 28.94; H, 4.37. Found: C, 28.91; H, 4.52%. Selected IR data (KBr): 3381mb, 2958m, 2927m, 2872m, 1630m, 1458m, 1389m, 1270w, 1125m, 1022s, 910m, 885w, 807w, 731m, 697w, 607m, 549sb, 410w cm⁻¹.

² Crystal structure data for **1**·3CH₂Cl₂: C₂₈H₅₁Mn₆Cl₉O₁₆, *M*_r = 1292.38, monoclinic, space group *P*2₁/*n*, *a* = 12.8051(10) Å, *b* = 17.3464(13) Å, *c* = 20.4713(15) Å, β = 96.688(2)°, *V* = 4516.2(6) Å³, *Z* = 4, ρ_{calcd} = 1.901 g cm⁻³, *T* = 173(2) K, 30334 reflections collected, 10320 unique (*R*_{int} = 0.0934), *R*₁ = 0.0503 and *wR*₂ = 0.1251, using 6251 reflections with *I* > 2σ(*I*).

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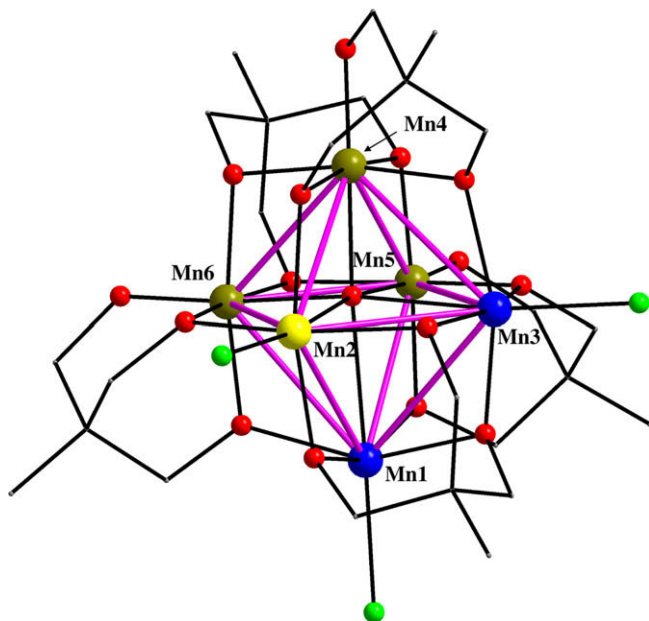


Fig. 1. Partially labeled representation of complex **1** with Mn–Mn vectors shown in purple to emphasize the Mn_6 octahedron. H atoms have been omitted for clarity. Colour scheme: Mn^{II} yellow; Mn^{III} blue; Mn^{IV} olive; O red; Cl green; C grey. (For interpretation of the references to colour in figure legends, the reader is referred to the web version of this article.)

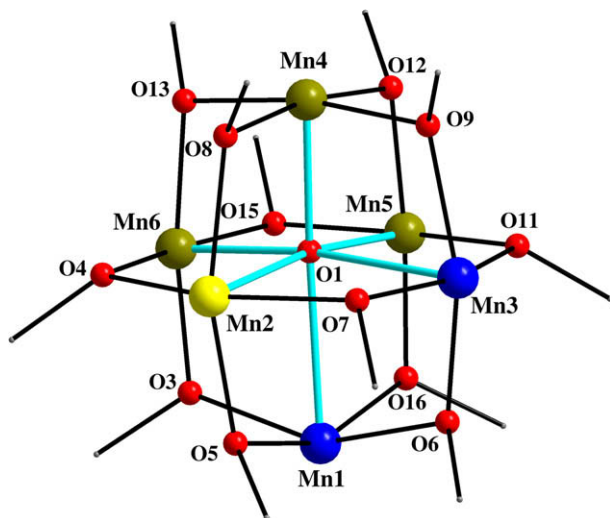


Fig. 2. Labeled PovRay representation of the complete $[Mn_6(\mu_6-O)(\mu-OR)_{12}]^{6+}$ core, emphasizing the central $[Mn_6(\mu_6-O)]^{18+}$ unit. Colour scheme as in Fig. 1.

Mn(1)–Mn(3), with the C_3 axis passing through central O1 and perpendicularly through the midpoint of the Mn(1)–Mn(3) triangular plane. Atoms Mn(1) and Mn(2) are thus related by a virtual mirror plane, and it is perhaps not unreasonable that they would be statically disordered about it. In fact, the virtual symmetry of the molecule is C_3 if we distinguish Mn^{III} atom Mn(3) from the disordered pair Mn(1)/Mn(2), the mirror plane passing through Mn(3), Mn(6), O(1), O(5) and O(12) (Fig. 2).

All Mn atoms are six-coordinate with distorted octahedral geometry, and only Mn(3) atom shows clearly the Jahn–Teller (JT) distortion expected for a high-spin, Mn^{III} (d^4) ion in near-octahedral geometry, taking the form of an axial elongation of the two *trans* Mn(3)–Cl(2) (2.329(1) Å) and Mn(3)–O(1) bonds (2.398(3) Å). There are no strong intermolecular hydrogen-bonds, only weak

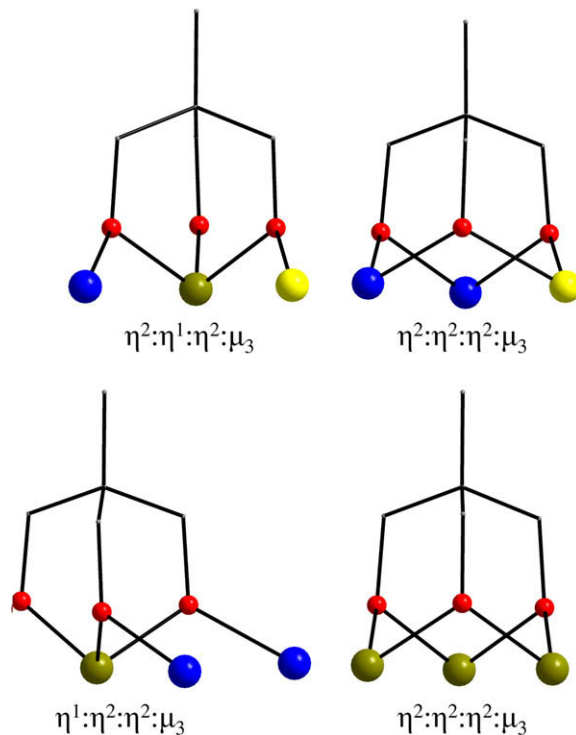


Fig. 3. The coordination modes of $thme^{3-}$ found in complex **1**. Colour scheme as in Fig. 1.

C–H...Cl contacts between C–H bonds of $thme^{3-}$ and lattice CH_2Cl_2 groups and the terminal Cl^- ions. Complex **1** is the first Mn_6 cluster at the Mn^{2+} , $2Mn^{3+}$, $3Mn^{4+}$ level, as well as a rare example of a hexanuclear molecular species with the $[M_6(\mu_6-O^{2-})]$ octahedral core [7], and the first in Mn coordination chemistry.

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 kOe (0.1 T). The $\chi_M T$ value steadily increases from 21.04 $cm^3 K mol^{-1}$ at 300 K to a maximum of 54.48 $cm^3 K mol^{-1}$ at 25 K, before dropping to 46.42 $cm^3 K mol^{-1}$ at 5.0 K (Fig. 4). The spin-only ($g = 2$) value for a non-interacting $[Mn^{II}-Mn_2^{III}Mn_3^{IV}]$ unit is 16.0 $cm^3 K mol^{-1}$. This indicates ferromagnetic exchange interactions within **1**, and the 25 K data strongly suggest a very large ground-state spin (S) value for the complex, with the sharp decrease at the lowest temperatures assigned to Zeeman ef-

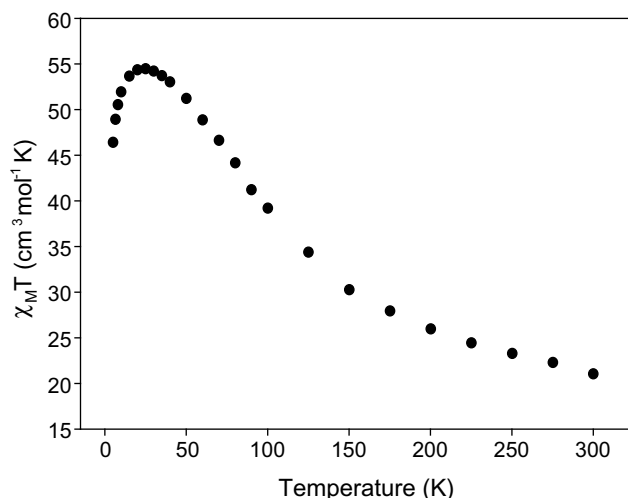


Fig. 4. $\chi_M T$ vs. T plot for **1** in a 1 kG field.

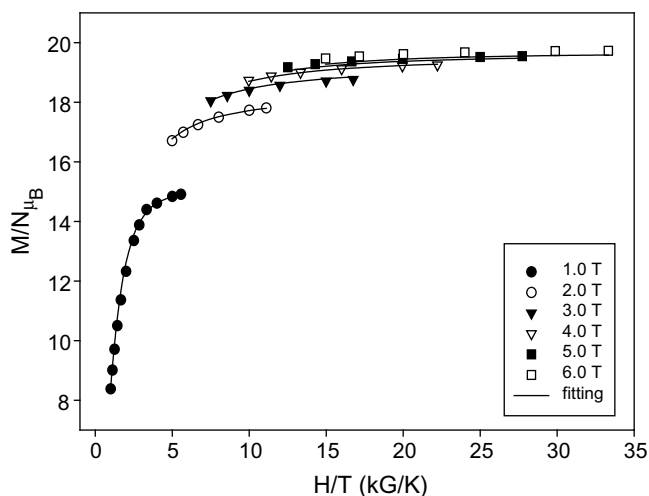


Fig. 5. Magnetization (M) vs. field (H) and temperature (T) data, plotted as reduced magnetization ($M/N\mu_B$) vs. H/T , for complex **1** at applied fields of 1.0–6.0 T and in the 1.8–10 K temperature range. The solid lines are the fit of the data; see the text for the fit parameters.

fects, zero-field splitting and/or weak intermolecular interactions. The 25 K value is consistent with an $S = 10$ or 11 ground state, the latter being the maximum possible, and a g value of 2.0 or slightly below, as expected for a $Mn^{II}/Mn^{III}/Mn^{IV}$ system [5]; the spin-only ($g = 2$) values for $S = 10$ and 11 state are 55 and 66 $\text{cm}^3 \text{K mol}^{-1}$.

In order to determine the ground state of **1**, magnetization (M) data were collected in the 1–6 T and 1.8–10.0 K ranges, and these are plotted as $M/N\mu_B$ versus H/T in Fig. 5. The data were fit by matrix-diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting (DS_z^2) and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Fig. 5) gave $S = 11$, $g = 1.97(2)$ and $D = -0.07(3) \text{ cm}^{-1}$, indicating a very high ground state spin with little magnetic anisotropy; an alternative fit with $S = 10$ is less favoured due to an unreasonable value for g of ~ 1.72 . We conclude that **1** has ground state of $S = 11$ and the small D value is consistent with the small content of JT-distorted Mn^{III} atoms within the molecule.

The $S = 11$ ground state was further supported by AC (alternating current) magnetic 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 and/or low-lying excited states. For **1**, the in-phase (χ'_M) AC signal, shown as $\chi'_M T$ in Fig. 6, 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 weak intermolecular interactions at lower temperatures, both dipolar and superexchange in nature) down to 0 K gives $\sim 60 \text{ cm}^3 \text{K mol}^{-1}$, indicating an $S = 11$ ground state with $g \sim 1.91$, in good agreement with the DC magnetization fits.

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 temperatures, magnetization versus dc field scans are required to be performed at low enough temperatures using the micro-SQUID apparatus [8]. Such studies are currently in progress and the corresponding results will be reported in due course.

In summary, the employment of the thme^{3-} ligand in higher oxidation state Mn cluster chemistry has yielded a mixed-valence-(II/III/IV) molecule with a $[Mn_6(\mu_6-O)]^{18+}$ octahedral core and a high $S = 11$ ground state. Note that the $S = 11$ for **1** is the maximum for a Mn^{II} , $2Mn^{III}$, $3Mn^{IV}$ species, indicating all interactions to be

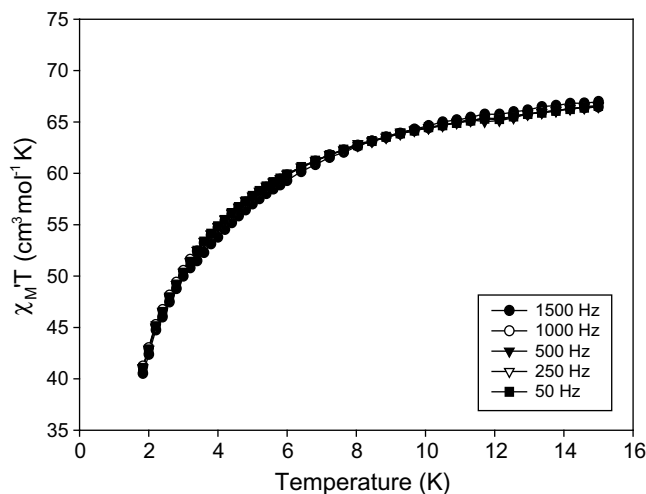


Fig. 6. Plot of the in-phase (χ'_M) as $\chi'_M T$ AC magnetic susceptibility vs. T in a 3.5 G field oscillating at the indicated frequencies for complex **1**.

ferromagnetic. This might at first glance seem strange for a complex that contains a Mn_3^{IV} triangular subunit, since $Mn^{IV}Mn^{IV}$ interactions are almost always antiferromagnetic, but note that the Mn^{IV} atoms are within a $[Mn_3(\mu_3-O)(\mu-O)_3]$ defect-cubane subunit involving bis-monoatomically-bridged $[Mn(\mu-O)_2Mn]$ pairs, and this results in acute $Mn^{IV}-O-Mn^{IV}$ angles ($95-101^\circ$) that can reasonably yield ferromagnetic interactions [9]. In fact, this is in accord with the ferromagnetic interactions seen within the central $[Mn_4^{IV}(\mu_3-O)_4]$ cubane of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes [9d], which have $Mn-O-Mn$ angles in the $95.0-100.7^\circ$ range. Similarly for the interactions in **1** between Mn^{IV} and Mn^{II} or Mn^{III} atoms, and interactions amongst the Mn^{II}/Mn^{III} atoms, which all again involve bis-monoatomically-bridged Mn_2 pairs and particularly acute $Mn-O^{2-}-Mn$ angles in the $89.19-90.62^\circ$ and $83.37-84.25^\circ$ ranges, respectively. A completely ferromagnetically coupled Mn_6 complex **1** is thus reasonable. These points will be analyzed in greater detail in the full paper.

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Appendix A. Supplementary data

CCDC 704395 contains the supplementary crystallographic data for **1** · $3CH_2Cl_2$. 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.2008.10.031.

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