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High Spin Molecules: Unusual Magnetic Susceptibility Relaxation Behavior of a Dodecanuclear Manganese Aggregate in Two Oxidation States

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HIGH SPIN MOLECULES: UNUSUAL MAGNETIC SUSCEPTIBILITY RELAXATION BEHAVIOR OF A DODECANUCLEAR MANGANESE AGGREGATE IN TWO OXIDATION STATES

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Abstract The mixed valence dodecanuclear complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_3]$ may be reduced by one electron to give $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$. Reduction of the complex occurs at one Mn^{III} ion to give an unusual trapped-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$ complex. This formulation is supported by X-ray crystallography at both low temperature and room temperature. DC (2.0–4.0 K, 20–50 kG fields) and AC (2.0–30 K, 1.0 and 0.0050 G fields, 25–1000 Hz frequencies) magnetic susceptibility measurements indicate ground states of $S=9$ and $S=19/2$ for the neutral and reduced species, respectively. $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$ exhibits an out-of-phase component of the AC magnetic susceptibility (χ''_M) which has a frequency dependent maximum. This is a very unusual property for a discrete molecular species to display. The neutral analog shows two peaks in the χ''_M vs. T plot. DC measurements also show the presence of prominent hysteresis loops, and field-cooled and zero-field-cooled magnetization data are not superimposed at low temperatures. The unusual magnetic relaxation properties persist even in polystyrene-doped samples of the complexes, indicating that this behavior arises from intramolecular rather than intermolecular properties.

INTRODUCTION

High spin molecules, both inorganic- and organic-based, have been actively sought as potential building blocks for molecule-based magnets. A particularly interesting class of molecules are the mixed valence $(\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4)$ complexes of general formula $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$.^{1–8} The synthesis of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**1**), the first of these complexes, was published over ten years ago.² The general structure is a $\text{Mn}^{\text{IV}}_4\text{O}_4$ cubane surrounded by a non-planar ring of 8 Mn^{III} ions, all strongly interconnected by a network of μ_3 -oxide bridges. The metal oxidation states are easily distinguished by the Jahn-Teller axial elongation of the Mn^{III} ions. We became interested in complexes of this type when a low yield synthesis of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$ (**2**) was obtained through a comproportionation reaction of $(\text{NBu}_4)[\text{MnO}_4]$ with $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ in the presence of benzoic acid.³ A high yield synthesis of this

compound was subsequently obtained through ligand substitution of complex **1** with benzoic acid. Both **1** and **2** show ground states with very large numbers of unpaired electrons ($S=9$ or $S=10$ in a 20 kG field, depending on the lattice solvent in the solid).¹

In addition to simple substitution of the carboxylate ligands, much more drastic changes to the core of the complex can be effected. Four Fe^{III} ions may be incorporated in place of four non-adjacent outer Mn^{III} ions to yield the complex $[\text{Fe}_4\text{Mn}_8(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$.⁴ The addition of an extra electron at each of the four Fe^{III} sites induces a large change in the magnetic interactions leading to an increased antiferromagnetic interaction overall and an $S=2$ ground state spin. In addition to metal substitution, all of the Mn_{12} complexes exhibit a chemically reversible one-electron reduction when examined by cyclic voltammetry.^{1,4} The reduction of **2** occurs at a readily accessible potential, and iodide is a sufficiently strong reducing agent for bulk generation of the reduced complex. Iodine is an easily separable by-product, and a variety of salts of $[\mathbf{2}]^-$ may be isolated.^{4a}

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ complexes have recently become the focus of increasing attention because of unusual AC magnetic susceptibility behavior,^{1,5} including the presence of a frequency dependent out-of-phase component (χ''_M). They exhibit a type of molecular hysteresis^{5,6} which was previously unknown in molecular complexes in which there is no evidence for long range magnetic order. This is believed to result from the high magnetic anisotropy of these molecules due to near-parallel alignment of the Jahn-Teller axes of the outer Mn^{III} ions.⁶ Because of fundamental interest in these dodecanuclear manganese aggregates, it was important to fully characterize a one-electron reduced species, and perform extensive DC and AC magnetic studies to test for the presence of these unusual molecular properties. Our recent results^{7,8} are described in this summary.

ISOLATION AND CHARACTERIZATION OF THE ONE-ELECTRON REDUCTION PRODUCT AND ITS NEUTRAL ANALOG

Initial attempts to crystallize the one-electron reduction product of **2** did not give X-ray quality crystals, thereby motivating further ligand substitution experiments to produce a range of Mn_{12} systems for characterization studies. The propionate derivative, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_3]$, (**3**) may be synthesized through the removal of MeCO_2H as a toluene azeotrope from the reaction of **1** with excess propionic acid. The neutral complex shows a chemically reversible reduction at 0.02 V vs. ferrocene/ferrocinium. Reduction of **3** with PPh_4I yields the stable complex, $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$ (**4**).

Both **3** and **4** have been crystallographically characterized.^{7,8} Bond distances and angles of complex **3** are quite unremarkable when compared to complexes **1** and **2**, which have been previously reported.^{2,3} An ORTEP representation of the anion of **4** is shown in Figure 1. In contrast to the three neutral examples, this anion contains one outer Mn ion that is no longer Jahn-Teller distorted and has equatorial bonds that are elongated by 0.2 Å relative to the neutral species, indicating the presence of one Mn^{II} ion (Mn 10 in Figure 1). It is quite unusual to see reduction of a Mn^{III} ion in preference to a Mn^{IV} ion. The formulation of the complex as a trapped-valence Mn^{II}Mn^{III}₇Mn^{IV}₄ makes it one of only two known complexes⁹ containing Mn^{II}, Mn^{III} and Mn^{IV} in the same molecule. The site of the reduction is perhaps determined by the rigidity of the core structure; if the reduction occurred at a Mn^{IV} site, Jahn-Teller distortion of that axial bond would create a great deal of strain in the central cubane unit. The outer Mn^{II} site is also ideally suited for coordination by two neutral water molecules which stabilize the lower oxidation state. An X-ray structure solution performed at 20°C confirms the trapped-valence formulation even at room temperature.

The observation of very similar paramagnetic solution NMR signals from both the neutral and the reduced complexes indicate intramolecular detrapping of the extra electron in **4** on the NMR timescale. Extensive NMR studies⁸ of the complexes indicate that the Mn₁₂O₁₂ core remains intact in solution and that both the neutral and reduced species are stable in solution indefinitely. There is also no intermolecular electron transfer that is fast

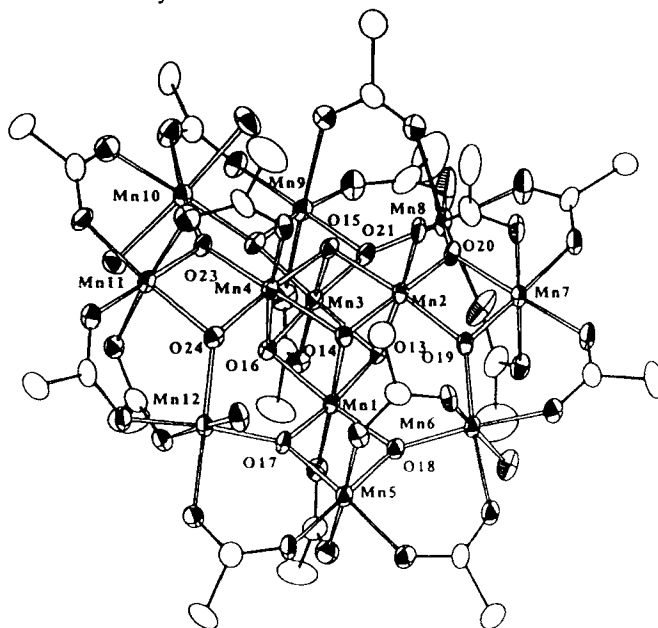


FIGURE 1. [Mn₁₂O₁₂(O₂CEt)₁₆(H₂O)₄]⁻

relative to the NMR timescale between neutral and reduced molecules in solution. However, there is evidence for intramolecular carboxylate and H₂O exchange. Complex **4** also exhibits a broad, low field X-band EPR signal at $g=10.5$ below a temperature of 60 K. Further characterization of the neutral and reduced species included conductivity measurements and elemental analyses. Further details of the characterization of these complexes are available elsewhere.⁸

MAGNETIC CHARACTERIZATION

DC Magnetic Susceptibility Studies

Measurements of the DC magnetic susceptibility of polycrystalline samples of complexes **3** and **4**, the purity of which were confirmed by elemental analysis and NMR spectroscopy. The samples were restrained in parafilm to prevent torquing, were made in a magnetic field of 10 kG. For complex **3**, χT vs. T data increase with decreasing temperature from 17.19 cm³ K mol⁻¹ (11.7 μ_B /molecule) at 320 K to 44.57 cm³ K mol⁻¹ (18.9 μ_B /molecule) at 20 K. Below 20 K, χT drops to a value of 26.6 cm³ K mol⁻¹ (14.6 μ_B /molecule) at 5 K, due to zero-field splitting effects. Complex **4** exhibits similar behavior, reaching a maximum of 43.0 cm³ K mol⁻¹ (18.5 μ_B /molecule) at 15 K. This type of behavior is indicative of a large number of unpaired electrons in the ground state.

To determine the ground states, magnetization data were collected at fields of 20-50 kG in the temperature range of 2.0-4.0 K. A large zero-field splitting effect is evidenced by the fact that the four isofield sets for both complexes are non-superimposable. Assuming that only one S state is populated at high field and low temperature, a least-squares fitting of the data yielded a best fit of $S=9$, $D=0.6$ cm⁻¹ and $g=1.95$ for complex **3**, and $S=19/2$, $D=0.4$ cm⁻¹ and $g=1.74$ for complex **4**. However, the slow relaxation effects present in these complexes at very low temperatures (*vide infra*) result in slow decay of the magnetization of the samples. Because the magnetization of the samples requires days to reach equilibrium after a decrease in temperature under these conditions, this could affect the accuracy of these fittings.

Low field magnetization data were also collected for **3** and **4** in a temperature range of 4.5-30 K at field strengths of 5, 10, 15, 20, and 25 G. For complex **3**, the data sets for the five different fields superimpose in the 13-19 K range, showing a broad maximum of $\chi_M T = 44.2$ cm³ K mol⁻¹, which corresponds to an $S=9$ ground state with $g = 1.98$. Similarly, for complex **4**, a maximum of $\chi T = 46.3$ cm³ K mol⁻¹ is reached between 6 and 12 K which corresponds to an $S=19/2$ ground state with $g = 1.93$.

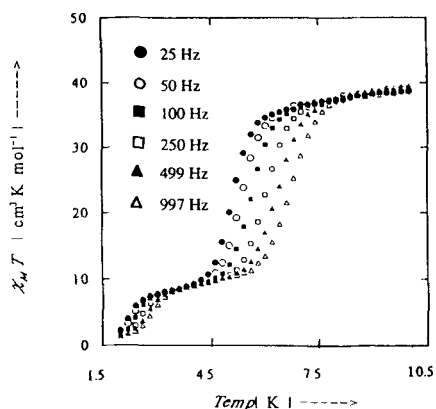


FIGURE 2. AC Susceptibility of Complex 3 ($\chi'_M T$) in the frequency range 25-997 Hz

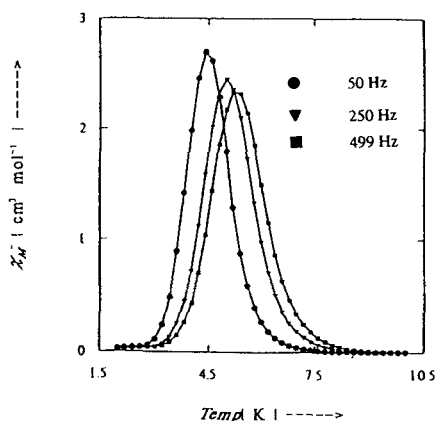


FIGURE 3. AC Susceptibility of Complex 4 (χ''_M) in the frequency range 50-499 Hz

AC Magnetic Susceptibility Studies

In an effort to further characterize the magnetic properties of **3** and **4**, AC magnetic susceptibility measurements were made with an oscillating field of 0.0050 G at frequencies of 25 to 997 Hz. Plots of $\chi'_M T$ for complex **3** (χ'_M is the real component of the susceptibility) vs. T show a relatively constant value of $\chi'_M T$ of $42.0 \text{ cm}^3 \text{K mol}^{-1}$ in the 11 - 23 K range. This corresponds to an $S=9$ ground state ($g=1.93$), which agrees with the low field DC data. At low temperatures, there is a two-step drop in $\chi'_M T$ at temperatures below 7 K. These data are shown in Figure 2. A drop may be due to relaxation processes, as described in previous work,¹ in which the molecule cannot remain in phase with the oscillating magnetic field. Complex **3**, however, exhibits two of these features, indicating the presence of two different relaxation processes. The out-of-phase (χ''_M) component shows two frequency dependent peaks corresponding to these two processes. Complex **4** shows similar behavior in the AC susceptibility; however, in an oscillating field of 1 G it exhibits only one drop in $\chi'_M T$ and only one frequency dependent peak in χ''_M . The out-of-phase component for complex **4** is shown in Figure 3.

Polymer doping of complex **3** was undertaken in order to indicate whether concentration effects would alter the AC susceptibility signals and in order to indicate whether the signals (especially the lower temperature one) were due to intramolecular effects or intermolecular magnetic phase transitions. Complex **3** and polystyrene (MW = 280,000) were dissolved in CH_2Cl_2 and then the solvent was evaporated to give a film. Two out-of-phase signals were seen from samples doped at 3.6 wt% and 54 wt% in polystyrene,

supporting the conclusion that both peaks are due to molecule-based phenomena.

Hysteresis Effects

Complexes **3** and **4** each exhibit large differences between zero-field cooled (ZFC) and field-cooled (FC) magnetization data. The data for complexes **3** and **4** are shown in Figure 4. For complex **3**, the temperature corresponding to the point where the ZFC and FC magnetization data become superimposed is 3.0 K, a temperature which coincides with the lowest temperature peak in the out-of-phase component of the AC susceptibility. For complex **4**, the two curves become superimposed above 4.6 K, the temperature for the maximum in the only out-of-phase component of the AC susceptibility for this complex. Complex **3** shows a hysteresis loop with a small coercive field of 310 G at 2.8 K when an applied magnetic field is cycled from 20 kG to -20 kG and then back to 20 kG. The hysteresis loop was present even when the experiment was performed on a polystyrene-doped sample, providing additional evidence for a molecular relaxation process. Complex **4** also exhibits a hysteresis loop with a much larger coercive field of 4062 G at 2.2 K; however, no hysteresis loop was seen at 2.8 K.

SUMMARY

Two new examples of the interesting class of compounds $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ have been isolated and fully characterized, including a complex which has been reduced by one-electron, **4**. Complex **4** is of special interest because it contains Mn^{II} , Mn^{III} and Mn^{IV} in the same molecule. The observation of “molecular hysteresis” in complexes **3** and **4** is quite unusual and is believed to result from the large magnetic anisotropies exhibited by the $\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4$ and $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$

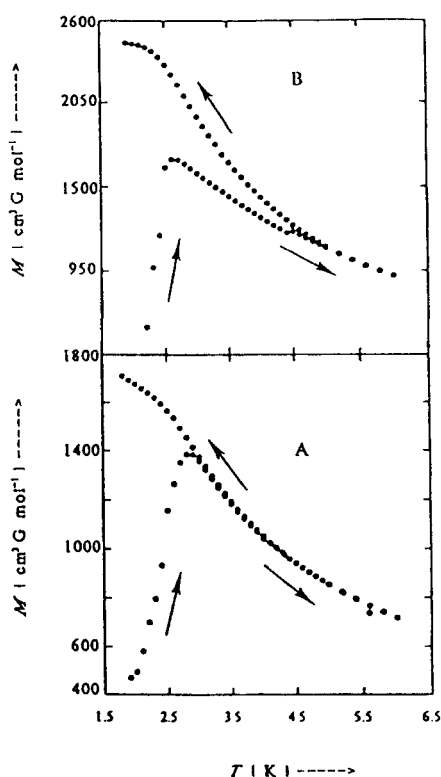


FIGURE 4. ZFC and FC Magnetization Data for **3** (A) and **4** (B).

complexes. Both **3** and **4** have high spin ground states ($S=9$ and $S=19/2$, respectively) and experience appreciable zero-field splitting, due to the single-ion zero field splitting of the Jahn-Teller distorted Mn^{III} ions. Approximately parallel alignment of the single-ion Jahn-Teller axes leads to a large magnetic anisotropy for the Mn_{12} molecules and resultant out-of-phase signals in the AC susceptibility. Because of the high degree of anisotropy, and hence the "bistability" of these molecules, the development of a new generation of molecule-based magnetic memory storage devices based on this molecular phenomenon may be possible. Attempts to isolate more examples of magnetically bistable molecules are underway so that we can improve our understanding of this important new area.

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