

## Superparamagnetic-like Properties of the Valence-trapped $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$ Anion in the Salt $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$

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Reduction of the  $8\text{Mn}^{\text{III}}, 4\text{Mn}^{\text{IV}}$  complex  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_3]$  with  $\text{PPh}_4$  in  $\text{CH}_2\text{Cl}_2$  leads to isolation of  $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$  (**3**) whose crystal structure shows that the added electron is localized on a formerly  $\text{Mn}^{\text{III}}$  ion to give a trapped-valence  $\text{Mn}^{\text{II}}, 7\text{Mn}^{\text{III}}, 4\text{Mn}^{\text{IV}}$  situation; DC and AC magnetic susceptibility studies show that **3** has an  $S = 19/2$  ground state and that it displays a superparamagnet-like non-zero, frequency-dependent, out-of-phase response in the AC susceptibility behaviour that is extremely unusual for a molecular species and unique for an ionic species.

Molecular complexes that have several metal ions and unpaired electrons are of importance within the realm of materials chemistry for understanding how large a metal ion cluster has to become in order to exhibit properties characteristic of extended lattices. Molecular complexes have the advantage of a single, crystallographically-defined size, unlike many nanoscale magnetic materials which have a distribution of cluster sizes.<sup>1</sup> Recently, Taft *et al.*<sup>2a</sup> and Papaefthymiou<sup>2b</sup> employed Mössbauer spectroscopy to demonstrate the presence of superparamagnetism<sup>3</sup> in  $\text{Fe}_{12}$  and  $\text{Fe}_{19}$  complexes. Similarly, only two molecular complexes,  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  [ $\text{R} = \text{CH}_3$  (**1**) or  $\text{Ph}$  (**2**)], have been reported<sup>4</sup> to exhibit out-of-phase AC susceptibility behaviour characteristic of superparamagnetic materials. This out-of-phase AC susceptibility signal has been shown<sup>5</sup> to arise from single  $\text{Mn}_{12}$  molecules that exhibit large magnetic anisotropy attributable to single-ion zero-field effects influencing an  $S = 10$  ground state.

In this communication, we report the preparation and characterization of  $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$  (**3**). This complex is interesting from several viewpoints, for it has a valence-trapped  $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$  anion in the solid state and it is the first ionic species to exhibit an out-of-phase AC susceptibility signal; the latter is particularly noteworthy since the presence of large cations ( $\text{PPh}_4^+$ ) between the paramagnetic anions suggests the observed properties are not intermolecular in origin.

A sample of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_3]$  (**4**) was prepared by the ligand-exchange reaction of complex **1** in toluene with an excess of  $\text{HO}_2\text{Cet}$ . The  $\text{MeCO}_2\text{H}$  was removed as the

toluene azeotrope and the product obtained as black crystals from toluene-hexanes in ~70% yield. The X-ray structure† of  $4 \cdot 4\text{H}_2\text{O}$  (not shown) confirms that complex **4** has essentially the same molecular structure as we reported<sup>4</sup> for complex **2**. Complex **4** consists of a central  $[\text{Mn}^{\text{IV}}_4\text{O}_4]^{8+}$  cubane held within a nonplanar ring of eight  $\text{Mn}^{\text{III}}$  ions by eight  $\mu_3\text{-O}^{2-}$  ions. Peripheral ligation is provided by sixteen  $\mu_2\text{-O}_2\text{Cet}^-$  and three terminal  $\text{H}_2\text{O}$  groups, one  $\text{Mn}^{\text{III}}$  ion being five-coordinate.

As we reported earlier for complexes **1** and **2**,<sup>4,6</sup> complex **4** exhibits four redox couples by cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$ . The first reduction is reversible with a potential of +0.02 V vs ferrocene, and the isolation of this reduced species has therefore been attempted and achieved. Addition of equimolar  $\text{PPh}_4\text{I}$  to complex **4** in  $\text{CH}_2\text{Cl}_2$  followed by addition of hexanes leads to small dark gold plates of complex **3** in 62% yield; crystallographically-suitable crystals were obtained from a  $\text{CH}_2\text{Cl}_2$ -hexanes layering. The X-ray structure‡ of **3** (Fig. 1) shows that the single added electron produces a valence-trapped  $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$  anion rather than a  $\text{Mn}^{\text{III}}_9\text{Mn}^{\text{IV}}_3$  one, *i.e.*, the site of reduction is an outer  $\text{Mn}^{\text{III}}$  ion of **4** rather than an inner  $\text{Mn}^{\text{IV}}$  ion. Manganese ion Mn(10) is clearly identified as a  $\text{Mn}^{\text{II}}$  ion on the basis of its characteristically longer bond distances (2.06–2.17 Å) relative to the other outer ( $\text{Mn}^{\text{III}}$ ) ions (1.86–1.99 Å for Jahn–Teller equatorial sites), the absence of a Jahn–Teller distortion as seen for the near-octahedral  $d^4$   $\text{Mn}^{\text{III}}$  ions, and the near congruency of the central  $[\text{Mn}_4\text{O}_4]$  cubane cores of **3** and **4**. Reduction of the central  $[\text{Mn}_4\text{O}_4]$  cubane would introduce a  $\text{Mn}^{\text{III}}$  ion into this unit, and its resulting Jahn–Teller axial elongation (or compression) would asymmetrically distort the cubane core. The consequent strain in the latter is presumably why reduction of a  $\text{Mn}^{\text{IV}}$  ion is disfavoured, and this represents our rationalization of the counterintuitive preferential reduction of a  $\text{Mn}^{\text{III}}$  ion vs a  $\text{Mn}^{\text{IV}}$  ion.

The DC-SQUID magnetic susceptibility characteristics of polycrystalline samples of complexes **3** and  $4 \cdot \text{H}_2\text{O}$  in a 10.0 kG

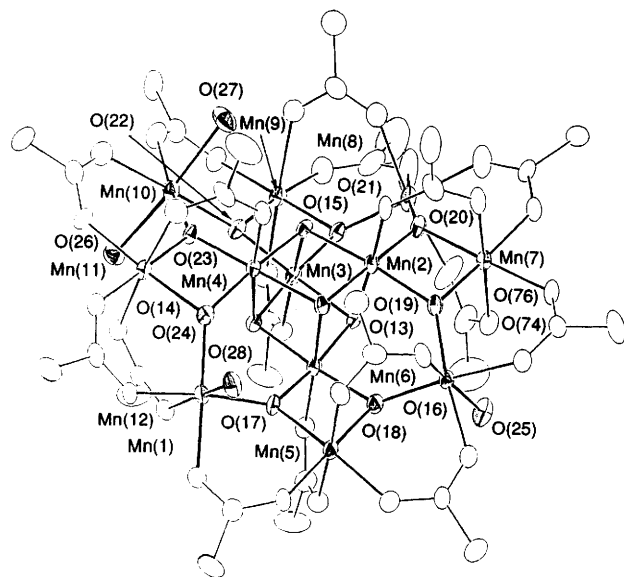


Fig. 1 ORTEP representation of the anion in  $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Cet})_{16}(\text{H}_2\text{O})_4]$  (**3**). Only the core atoms are labelled. The atom Mn(10) is the single  $\text{Mn}^{\text{II}}$  ion in this  $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_7\text{Mn}^{\text{IV}}_4$  anion.

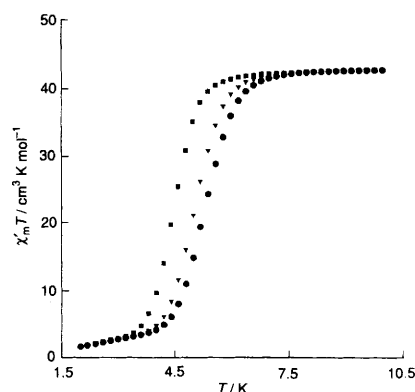


Fig. 2 Plot of the AC  $\chi'_m T$  vs  $T$  for a polycrystalline sample of complex **3**. Data were collected at three frequencies: (●) 50; (▼) 250; and (■) 500 Hz.

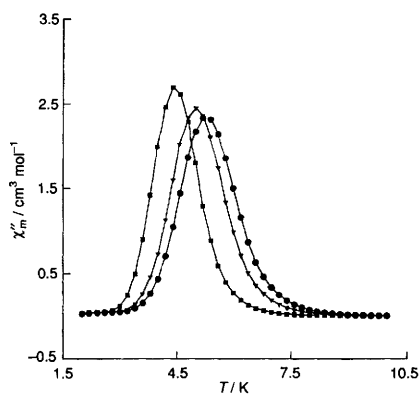


Fig. 3 Plot of the molar out-of-phase AC susceptibility  $\chi''_M$  vs  $T$  for a polycrystalline sample of  $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{Ct})_{16}(\text{H}_2\text{O})_4]$  (4). The measurements were carried out at three different frequencies: (●) 50; (▼) 250; and (■) 500 Hz. The lines are included as a visual aid.

field, from a plot of  $\chi_M T$  vs  $T$ , gave values of  $\chi_M T$  at 320.0 K of 16.89 and 17.19  $\text{cm}^3 \text{K mol}^{-1}$ , respectively, which correspond to  $\mu_{\text{eff}}$  values of 11.62 and 11.73 for complexes 3 and 4·H<sub>2</sub>O. It can be seen that a decrease in temperature of either 3 or 4·H<sub>2</sub>O leads to a dramatic increase in  $\chi_M T$  below 100 K, with a maximum at ~20 K for both complexes. This temperature dependence, similar<sup>4</sup> to that for complexes 1 and 2, is diagnostic of the population of a ground state with a relatively large spin.

In order to determine the ground state spin for complexes 3 and 4·H<sub>2</sub>O, magnetization data were collected under a variety of conditions. DC-SQUID data were obtained in the 5–300 K range at several magnetic fields from 5 G to 50 kG. AC-SQUID data were also run in the 2.0–30 K range in fields of 1.0 and 0.0050 G and at frequencies in the 25–1000 Hz range. An analysis of all the data for the neutral complex 4·H<sub>2</sub>O shows that this  $\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4$  complex has an  $S = 9$  ground state (maximum in  $\chi_M T$  of ~43  $\text{cm}^3 \text{K mol}^{-1}$  at low temperatures and fields). The benzoate complex 2 was also found to have an  $S = 9$  ground state using low-field AC susceptibility data, whereas the acetate complex 1 was found to have an  $S = 10$  ground state. All of the DC- and AC-SQUID data for complex 3 indicate that the  $\text{Mn}_{12}$  anion in this salt has an  $S = 19/2$  ground state. Thus, the  $\text{Mn}_{12}$  anion in 3 has a ground state with 19 unpaired electrons, while the ground state of the neutral propionate complex 4·H<sub>2</sub>O has 18 unpaired electrons.

The most interesting properties of the above complexes are revealed in zero-field AC susceptibility measurements. In Fig. 2 is given a plot of  $\chi'_M T$  vs  $T$  for complex 3, where  $\chi'_M$  is the in-phase component of the AC susceptibility measured at a field of 1.00 G (similar data were obtained at 0.0050 G). Experimental data are shown for three different frequencies (50, 250 and 500 Hz) in the range of 2.00–10.0 K (measurements were made up to 30.0 K). The AC  $\chi'_M T$  values exhibit a plateau in the ~6–16 K range, below which there is an abrupt decrease in  $\chi'_M T$  as  $T$  is decreased. This abrupt decrease is due to relaxation effects associated with anisotropy in the Zeeman interaction.

Fig. 3 shows the origin of the abrupt decrease in AC  $\chi'_M T$  values. The value of the out-of-phase component of the AC susceptibility,  $\chi''_M$ , is plotted vs  $T$  for complex 3. At low temperatures, there is a non-zero value of  $\chi''_M$  which is frequency-dependent. Maxima are seen at 4.4, 5.0 and 5.2 K at frequencies of 50, 250 and 500 Hz, respectively. The only other molecular complexes for which non-zero  $\chi''_M$  values have been reported<sup>4</sup> are complexes 1 and 2. The  $\chi''_M$  values for these two complexes are also frequency-dependent, where, for example, maxima are seen<sup>4</sup> for complex 1 at 5.5, 5.9, and 6.8 K for frequencies of 55, 100, and 500 Hz, respectively. The magnitudes of the  $\chi''_M$  signals for complex 3 are less than those for complexes 1 and 2.

The observation of an out-of-phase AC susceptibility for molecular complexes 1 and 2, and the salt 3 is extremely unusual. The magnetic moment of a simple molecular paramagnet would readily be able to track the oscillating magnetic field in the AC experiment. The non-zero  $\chi''_M$  values shown in Fig. 3 mean that when the magnetic field is oscillating at a frequency in the 50–500 Hz range, the magnetic moment of an individual  $\text{Mn}_{12}$  anion cannot keep in phase with the oscillating field. An out-of-phase susceptibility component develops. Frequency-dependent  $\chi''_M$  values have been noted<sup>7</sup> previously for superparamagnetic materials. Superparamagnetism occurs in single-domain magnetic materials (e.g. oxides), where there are extended arrays of exchange-interacting ions.

The likely origin of non-zero  $\chi''_M$  values for complexes 1, 2 and 3 lies in the presence of single-ion interactions for the high-spin  $\text{Mn}^{\text{III}}$  ions (Jahn–Teller distorted) which accumulate to give a very appreciable zero-field splitting in the  $S = 9$  (or 10) or  $S = 19/2$  ground states. Thus, there is a large magnetic anisotropy for each  $\text{Mn}_{12}$  anion in complex 3. Single-crystal measurements<sup>5</sup> for complex 1 show that there is an appreciable hysteresis in magnetization at 2.2 K. Because there is slow relaxation at these low temperatures, the possibility of molecular bistability exists. The present measurements demonstrate that complex 3 shows an out-of-phase AC susceptibility like complexes 1 and 2 even though 3 has, compared with 1 and 2, reduced symmetry (one  $\text{Mn}^{\text{II}}$  ion) and large  $\text{PPh}_4^+$  cations which provide significant additional insulation between the  $\text{Mn}_{12}$  units. This suggests that the novel properties of this type of species are indeed *intramolecular* rather than *intermolecular* in origin.

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## Footnotes

† Details will be provided in the full paper. Dried sample analyses for 4·H<sub>2</sub>O.

‡ Crystallographic data for 3 at –168 °C: monoclinic,  $P2_1/c$ ,  $a = 13.046(4)$ ,  $b = 28.223(9)$ ,  $c = 27.162(8)$  Å,  $\beta = 96.32(1)^\circ$ ,  $Z = 4$ ,  $V = 9940.4$  Å<sup>3</sup>;  $R(R_w) = 6.51$  (6.65)% using 9871 unique reflections with  $I > 3\sigma(I)$ . All non-hydrogen atoms were refined anisotropically, except eight atoms, with varying occupancy factors, of a disordered solvent molecule. There was also some positional disorder between one propionate, O(74), and one H<sub>2</sub>O group, O(25). In 35% of the molecules, O(25) is a propionate oxygen and O(74) is a water oxygen; corresponding occupancies for the propionate carbon atoms in the space between these oxygen atoms were observed. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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