A third isolated oxidation state for the Mn$_{12}$ family of single-molecule magnets

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Dianionic members of the Mn$_{12}$ family of single-molecule magnets have been prepared by two-electron reduction of the neutral cluster; the [PPh$_4$]$_2$[Mn$_{12}$O$_{12}$(O$_2$CR)$_{16}$(H$_2$O)$_4$] representative has been shown to possess an S = 10 ground state and to exhibit out-of-phase ac susceptibility signals diagnostic of single-molecule magnetism behavior. An exciting development in nanoscale magnetic materials occurred in 1993 when [Mn$_{12}$O$_2$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] I was identified as a nanoscale magnet, 1 the first to comprise discrete, (magnetically) non-interacting molecular units rather than a 3D extended lattice (metals, metal oxides, etc.). This initiated the field of molecular nanomagnetism and such a molecule has been termed a single-molecule magnet (SMM). 2 Other [Mn$_{12}$O$_2$(O$_2$CR)$_{16}$(H$_2$O)$_4$] (R = Et, Ph, etc.; x = 3 or 4) derivatives have since been studied, 1, 3 and they display similar properties. SMM behavior is due to a combination of a large ground state spin (S) of S = 10 and negative (easy axis) magnetization as gauged by a negative zero-field splitting parameter D. As a result, there is a significant barrier for the relaxation of the cluster’s magnetization vector, and these Mn$_{12}$ molecules are thus magnetizatn magnets.

More recently, the one-electron reduced complex [NPr$_n$][Mn$_{12}$O$_2$(O$_2$CEt)$_{16}$(H$_2$O)$_4$] and related species with S = 19/2 ground state have also been found to be SMMs. 3 In addition, new examples of SMMs have been found in the family of [Mn$_n$O$_n$X(O$_2$CMe)$_{dm}(dbm)$_n$] (X = Cl$^-$, Br$^-$, F$^-$, N$_3^-$, MeCO$_2$$^-$, etc.) complexes containing a [Mn$_n$(O$_2$)$_n$(X$_n$)$_n$] core and an S = 9/2 ground state. 4, 5 as well as a few other species. 6, 7 Here, we report that the two-electron reduced form of the [Mn$_{12}$] complexes has been successfully isolated and that this retains both a high ground state S value and the SMM properties of the [Mn$_{12}$]$_{2}^-$(NO$_2$)$_2^-$ species. This extends the Mn$_{12}$ of SMMs to a third oxidation level and provides an invaluable new datum point for our future understanding of how changing spin and magnetic anisotropy can affect the properties of these important molecules. We herein report the synthesis and characterization of the new [Mn$_{12}$O$_2$(O$_2$CR)$_{16}$(H$_2$O)$_4$]$^+$ species.

[Mn$_{12}$O$_2$(O$_2$CR)$_{16}$(H$_2$O)$_4$] complexes with electron-withdrawing groups [R = CHCl$_2$ (2), C$_6$F$_5$ (3)] to facilitate multi-electron reduction were prepared from using the procedure reported elsewhere. 1, 3 The representative reducing agent, as employed for one-electron reductions. 3 Thus, [Mn$_{12}$O$_2$(O$_2$CR)$_{16}$(H$_2$O)$_4$] derivatives. The dianionic species were therefore prepared from [Mn$_{12}$O$_2$(O$_2$CEt)$_{16}$(H$_2$O)$_4$] representative has been shown to possess an S = 10 ground state and to exhibit out-of-phase ac susceptibility signals diagnostic of single-molecule magnetism behavior.

Fig. 1 Cyclic voltammogram at 100 mV s$^{-1}$ for complex 2 in MeCN containing 0.10 M NBu$_4$PF$_6$ as supporting electrolyte. The working and auxiliary electrodes were glassy carbon and Pt wire, respectively. The indicated potentials are vs. ferrocene as an internal reference.

Table 1 Electrochemical data for [Mn$_{12}$O$_2$(O$_2$CR)$_{16}$(H$_2$O)$_4$] complexes a

<table>
<thead>
<tr>
<th>R</th>
<th>$E'_1/N^0$</th>
<th>$E'_2/N^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>0.18</td>
<td>-0.06</td>
</tr>
<tr>
<td>CH$_2$Cl</td>
<td>0.60</td>
<td>0.30</td>
</tr>
<tr>
<td>CHCl$_2$</td>
<td>0.91</td>
<td>0.61</td>
</tr>
<tr>
<td>C$_6$F$_5$</td>
<td>0.12</td>
<td>-0.23</td>
</tr>
<tr>
<td>C$_6$H$_5$NO$_2$-</td>
<td>0.47</td>
<td>0.19</td>
</tr>
<tr>
<td>C$_6$H$_4$NO$_2$-</td>
<td>0.49</td>
<td>0.23</td>
</tr>
<tr>
<td>C$_6$H$_5$(NO$_2$)$_2$-</td>
<td>0.74</td>
<td>0.45</td>
</tr>
<tr>
<td>C$_6$F$_5$(NO$_2$)$_2$-</td>
<td>0.64</td>
<td>0.46</td>
</tr>
</tbody>
</table>

a In MeCN, unless otherwise indicated; values are DPV peak potentials vs. ferrocene. $^b$ First reduction; $^c$ Second reduction; $^d$ In CH$_2$Cl$_2$.  

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and 1.80–4.00 K ranges (Fig. 3). Fitting of the data gave $S = 10$, $D = -0.27 \text{ cm}^{-1}$ ($-0.39 \text{ K}$) and $g = 2.00$. The ground state spin is thus similar to the $S = 10$ and 19/2 values for the neutral and monoanionic complexes, respectively. This suggested that the dianionic complexes might also be SMMs, i.e. show slow magnetization relaxation (reorientation) rates, and this was confirmed in ac susceptibility studies by an out-of-phase signal ($\chi''$) in the 2–3 K range (Fig. 4, bottom). ac Susceptibility studies monitor the response of a material’s magnetization (magnetic moment) to an applied, oscillating field, and a non-zero $\chi''$ signal shows that the magnetization cannot relax fast enough to keep in-phase with the oscillating field. The positions of the $\chi''$ peaks, at which temperature the relaxation rate equals the ac frequency, are in the 2–3 K range, lower than the 4–6 and 6–8 K ranges for the $\chi''$ peaks in the monoanionic and neutral complexes, respectively (Fig. 4). This is consistent with the changing $S$ and $D$ values on progressive reduction since the barrier to thermally-activated reversal of the magnetization direction is related to $\Delta D$ and $(S(S+1))$ for integer and half-integer spins, respectively. The $S(D)$ values for the three oxidation levels are: [Mn$_{12}$] $10 \ (= -0.5 \text{ cm}^{-1})$; [Mn$_{12}$]$^{2+} \ 19/2 \ (= -0.4 \text{ cm}^{-1})$; [Mn$_{12}$]$^{3-} \ 10 \ (= -0.3 \text{ cm}^{-1})$.

In conclusion, the [Mn$_{12}$] family of SMMs now provides three oxidation levels for the study of this important new phenomenon. In particular, the [Mn$_{12}$]$^{2+}$ vs. [Mn$_{12}$] comparison provides an invaluable opportunity to study how the magnetic properties and quantum tunneling behaviour of equivalent spin ($S = 10$) systems vary with changing magnetoanisotropy.

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Notes and references

1 Complexes 5–7 have been fully characterized by NMR, IR, CV and elemental analysis (C, H, N).
2 Crystal data: 5\·CH$_2$Cl$_2$·H$_2$O: C$_{44}$H$_{34}$Cl$_{18}$Mn$_{12}$O$_{8}$P$_2$, $M_r = 4166.79$, triclinic, space group $P\overline{1}$, $a = 15.153(2)$, $b = 21.858(2)$, $c = 22.130(2)$ Å, $\alpha = 109.45(1)$, $\beta = 93.78(1)$, $\gamma = 96.52(1)^\circ$, $U = 6824$ Å$^3$, $Z = 2$, $T = 115K$, $\mu$(Mo-K$\alpha$) = 19.7 mm$^{-1}$, 146767 reflections measured, 31965 unique ($R_p = 0.129$, $R(F) = 0.0636$, $R_{wp}(F) = 0.0553$ using 12440 unique reflections with $I > 2\sigma(I)$). CCDC 182/1822. See http://www.rsc.org/suppdata/cc/b0/b006519f/ for crystallographic files in .cif format.