# 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 $[PPh_4]_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ 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 $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ **1** 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 $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ (R = Et, Ph, *etc.*; $x$ = 3 or 4) derivatives have since been studied,[1,3] and they display similar properties. SMM behaviour is due to a combination of a large ground state spin ($S$) of $S$ = 10 and negative (easy axis) magnetoanisotropy 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 magnetizable magnets.

More recently, the one-electron reduced complex $[NPr_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ and related species with $S$ = 19/2 ground states have also been found to be SMMs.[3] In addition, new examples of SMMs have been found in the family of $[Mn_4O_3X(O_2CMe)_3(dbm)_3]$ (X = $Cl^-$, $Br^-$, $F^-$, $N_3^-$, $MeCO_2^-$, *etc.*) complexes containing a $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}X)]^{6+}$ core and an $S$ = 9/2 ground state,[2,4] as well as a few other species.[5–7] 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 $[Mn_{12}]^{0,-}$ 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 state and magnetic anisotropy can affect the properties of these important molecules. We herein report the synthesis and characterization of the new $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{2-}$ species.

$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes with electron-withdrawing groups [R = $CHCl_2$ (**2**), $C_6F_5$ (**3**), $C_6H_3(NO_2)_2$-2,4 (**4**), *etc.*] to facilitate multi-electron reduction were prepared from **1** using the procedure reported elsewhere.[1,3] The representative CV in MeCN of **2** (Fig. 1) shows three quasi-reversible one-electron reduction processes at 0.91, 0.61 and 0.29 V *vs.* ferrocene, and a fourth irreversible reduction at lower potential. These values are significantly more positive than for the R = Me and Ph derivative (Table 1).[1,3] In addition, the second and third reductions appear more reversible by electrochemical criteria (peak currents and separations) than those for previous $[Mn_{12}]$ derivatives. The dianionic species were therefore targeted and successfully prepared on a large scale using $I^-$ as reducing agent, as employed for one-electron reductions.[3] Thus, addition of 2 equivalents of $NPr^n_4I$ or $PPh_4I$ in MeCN, removal of solvent and recrystallization from MeCN–$Et_2O$–hexanes or $CH_2Cl_2$–hexanes gave dark red–brown $[PPh_4]_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ **5**, $[NPr^n_4]_2[Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4]$ **6** and $[NPr^n_4]_2[Mn_{12}O_{12}(O_2CC_6H_3(NO_2)_2\text{-}2,4)_{16}(H_2O)_4]$ **7**,† as well as others [eqn. (1)].

$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + 2NPr^n_4I \rightarrow [NPr^n_4]_2[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + I_2 \qquad (1)$$

The structure‡ of the dianion of **5** (Fig. 2) confirms the same structure as in the neutral and monoanionic species, but now with a $2Mn^{II}$, $6Mn^{III}$, $4Mn^{IV}$ description indicating that the two added electrons are on outer $Mn^{II}$ (formerly $Mn^{III}$) ions (Mn9 and Mn11 of Fig. 2) rather than $Mn^{IV}$ ions in the cubane, as found in the one-electron reduced complexes,[3] which are $Mn^{II}$, $7Mn^{III}$, $4Mn^{IV}$. The assignment of $Mn^{II}/Mn^{III}/Mn^{IV}$ is based on relative Mn–O distances, bond valence sum calculations, and Jahn–Teller (JT) axial elongations only on six Mn sites. $^1H$ NMR studies in solution are consistent with electron-detrapping amongst the outer eight Mn ions on the NMR timescale, as also found for the mono-anionic species.[3]

The ground state of **5** was determined from reduced magnetization ($M/N\mu_B$) *vs.* $H/T$ measurements in the 10–70 kG

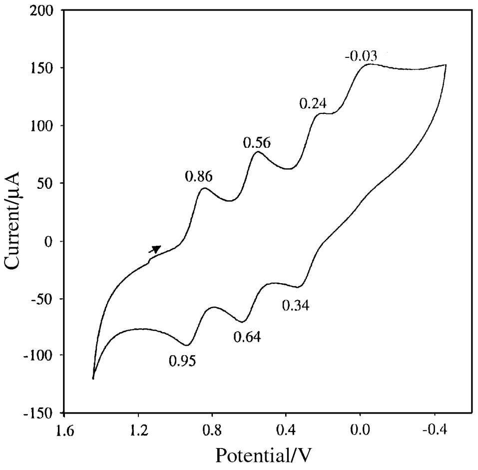

**Fig. 1** Cyclic voltammogram at 100 mV $s^{-1}$ for complex **2** in MeCN containing 0.10 M $NBu^n_4PF_6$ as supporting electrolyte. The working and auxiliary electrodes were glassy carbon and Pt wire, respectively. The indicated potentials are *vs.* ferrocene as an internal reference.

**Table 1** Electrochemical data for $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes[a]

| R | $E_1$/V[b] | $E_2$/V[c] |
|---|---|---|
| $CH_3$ (**1**) | 0.18 | −0.06 |
| $CH_2Cl$ | 0.60 | 0.30 |
| $CHCl_2$ (**2**) | 0.91 | 0.61 |
| $C_6H_5$[d] | 0.12 | −0.23 |
| $C_6H_4NO_2$-2 | 0.47 | 0.19 |
| $C_6H_4NO_2$-4 | 0.49 | 0.23 |
| $C_6H_3(NO_2)_2$-2,4 (**4**) | 0.74 | 0.45 |
| $C_6F_5$ (**3**) | 0.64 | 0.46 |

[a] In MeCN, unless otherwise indicated; values are DPV peak potentials *vs.* ferrocene. [b] First reduction. [c] Second reduction. [d] In $CH_2Cl_2$.

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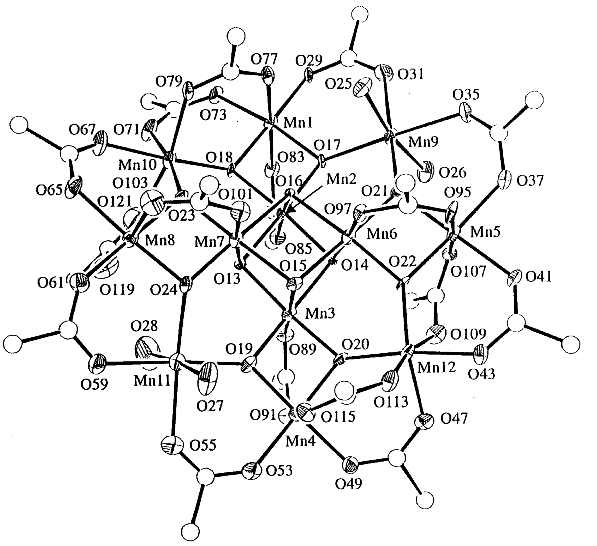

**Fig. 2** ORTEP representation of the anion of complex **5** showing 50% probability ellipsoids. For clarity, all H and Cl atoms have been omitted.

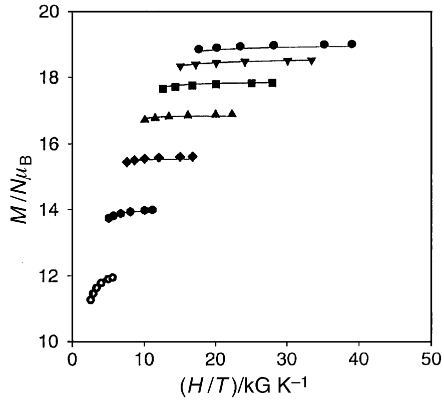

**Fig. 3** Plot of $(M/N\ \mu_B)$ *vs.* $H/T$ for complex **5** at 10 (⊕), 20 (•), 30 (◆), 40 (▲), 50 (■), 60 (▼) and 70 (●) kG. The solid lines are fits using the appropriate method;[9] see text for the fit parameters.

and 1.80–4.00 K ranges (Fig. 3). Fitting of the data gave $S = 10$, $D = -0.27$ cm$^{-1}$ ($-0.39$ 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 ($\chi_m''$) 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 $\chi_m''$ signal shows that the magnetization cannot relax fast enough to keep in-phase with the oscillating field. The positions of the $\chi_m''$ 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 $\chi_m''$ 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 $S^2|D|$ and $(S^2 - \frac{1}{4})|D|$ for integer and half-integer spins, respectively. The $S(D)$ values for the three oxidation levels are: [Mn$_{12}$], 10 ($\approx -0.5$ cm$^{-1}$); [Mn$_{12}$]$^-$, 19/2 ($\approx -0.4$ cm$^{-1}$); [Mn$_{12}$]$^{2-}$, 10 ($\approx -0.3$ 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.

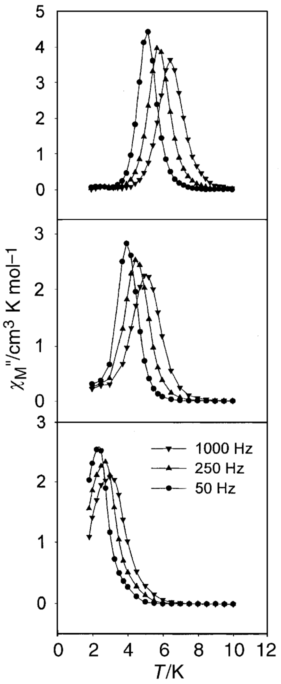

**Fig. 4** Plot of the out-of-phase ac susceptibility ($\chi_m''$) for complex **2** (top), [NPr$^n_4$][Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_{16}$(H$_2$O)$_4$] (middle) and complex **5** (bottom) at the indicated oscillation frequencies of the applied field.

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## Notes and references

† Complexes **5**–**7** have been fully characterized by NMR, IR, CV and elemental analysis (C, H, N).

‡ *Crystal data*: **5**·4CH$_2$Cl$_2$·H$_2$O: $C_{84}H_{74}Cl_{40}Mn_{12}O_{59}P_2$, M$_r$ = 4166.79, triclinic, space group $P\bar{1}$, $a = 15.153(2)$, $b = 21.858(2)$, $c = 22.130(2)$ Å, $\alpha = 109.45(1)$, $\beta = 93.78(1)$, $\gamma = 96.52(1)°$, $U = 6824$ Å$^3$, $Z = 2$, $T =$ 115K, $\mu$(Mo-K$\alpha$) = 19.7 mm$^{-1}$, 146767 reflections measured, 31965 unique ($R_{av} = 0.129$), $R(F) = 0.0638$, $R_w(F) = 0.0551$ using 12440 unique reflections with $I > 2.33\sigma(I)$.

CCDC 182/1822. See http://www.rsc.org/suppdata/cc/b0/b006519f/ for crystallographic files in .cif format.

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