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A new synthetic method to Mn carboxylate clusters: reductive fragmentation of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ to $[Mn_8O_2(O_2CR)_{14}(RCO_2H)_4]$ (R = CH_2Bu^t)

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The reaction of $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(H_2O)_4]$ (1) with a reducing agent followed by recrystallization from CH_2Cl_2/$MeNO_2$ affords the novel octanuclear complex $[Mn_8O_2(O_2CCH_2Bu^t)_{14}(Bu^tCH_2CO_2H)_4]$ (2).

There is currently considerable interest in new polynuclear Mn complexes, inspired by their potential to act as single-molecule magnets (SMMs).[1] SMMs possess a significant energy barrier to relaxation (reorientation) of their magnetization direction. This results from a combination of two molecular properties: a large spin (S) and a large easy-axis type magnetoanisotropy (negative axial zero-field splitting parameter, D). The upper limit of the energy barrier to reorientation is given by $S^2|D|$ or $(S^2–\frac{1}{4})|D|$ for integer and non-integer spins, respectively. The SMMs with the largest energy barrier to date are the Mn_{12} family of complexes $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ (x = 3 or 4) with S = 10. SMMs are promising candidates for future applications in data storage and other areas; however, species with larger energy barriers are necessary. This implies molecules with larger spin and/or anisotropy, and one route to these is the synthesis of new high nuclearity Mn complexes.

A synthetic methodology that has proven useful for this in the past is the aggregation to higher nuclearity products of preformed Mn carboxylate clusters, triggered by carboxylate abstraction,[2] electron transfer,[3] incorporation of dicarboxylates,[4] *etc.* For example, reduction of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ gives $[Mn_6O_2(O_2CPh)_{10}(py)_2(MeCN)_2]$ (**3**);[3] it has been proposed that reduction of the $[Mn^{II}Mn^{III}_2]$ unit in the former affords the $[Mn^{II}_2Mn^{III}]$ analogue, which is unstable and undergoes aggregation to the hexanuclear product. Over the last decade or so, a large number of high nuclearity Mn clusters (= Mn_8) have been prepared, and it has become pertinent to ask whether these might themselves prove good starting materials to new clusters, with higher or lower nuclearities. The Mn_{12} family of complexes are particularly attractive for this. Herein, we report the proof-of-feasibility of this approach, which comprises the synthesis, crystal structure and magnetic characterization of a new $Mn^{II}_6Mn^{III}_2$ octanuclear cluster $[Mn_8O_2(O_2CCH_2Bu^t)_{14}(Bu^tCH_2CO_2H)_4]$ (**2**). The synthesis of **2** involves reductive destabilization of $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(H_2O)_4]$ (**1**) followed by structural rearrangement.

Complex **2** was initially prepared by the reaction of **1**[5] (0.18 mmol) with pyridine-2,6-dimethanol ($pdmH_2$) (0.54 mmol) in CH_2Cl_2 (20 cm^3) for 16 h. The resulting solution was filtered through celite, reduced in volume to *ca.* 5 cm^3, and layered with two volumes of $MeNO_2$. After one week, crystals of **2**.$pdmH_2$ were isolated in 40% yield.‡ An analogous procedure employing phenol in place of $pdmH_2$ also gave **2**, as confirmed by infrared spectroscopy.

The reaction involves reduction of the Mn from an average oxidation state of +3.33 in **1** ($Mn^{III}_8Mn^{IV}_4$) to an average oxidation state of +2.25 in **2** ($Mn^{II}_6Mn^{III}_2$). This is accomplished by the $pdmH_2$, which is concomitantly oxidized, as has been observed previously in the formation of other Mn–carboxylate clusters, for example $[Mn_4(O_2CMe)_2(pdmH)_6]^{2+}$.[6] However, in the present case the $pdmH_2$ is not incorporated in the product and, in fact, alternative reducing agents such as phenol may be used instead. Although both one- and two-electron reduced $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ species have been prepared and isolated,[7] it appears that excessive reduction destabilizes the Mn_{12} structure, which then undergoes structural fragmentation and rearrangement to give complex **2**.

The crystallization of pure **2** requires the $Bu^tCH_2CO_2^-$/$MeNO_2$ combination. The use of precipitating solvents other than $MeNO_2$ in the described procedure, or the reduction of Mn_{12} complexes possessing other carboxylates (*e.g.* $MeCO_2^-$) and recrystallization from CH_2Cl_2/$MeNO_2$, both give materials that, by infrared spectroscopy and preliminary X-ray characterization, are neither **2** nor structural analogues of **2** with other carboxylates. On the other hand, **2** can also be isolated by replacing CH_2Cl_2 in the original synthesis with $CHCl_3$. A similar sensitivity to ligand/solvent has been observed previously with the $Bu^tCH_2CO_2^-$/$MeNO_2$ combination. We have recently reported that recrystallization of **1** from CH_2Cl_2/$MeNO_2$ affords $[Mn_{30}O_{24}(OH)_8(O_2CCH_2Bu^t)_{32}(H_2O)_2(MeNO_2)_4]$.[8] This transformation has also been found to occur only with complex **1** among the Mn_{12} family, and only in the presence of $MeNO_2$. In both this and the present reaction, it appears that the combination of the hydrophobic $^tBuCH_2CO_2^-$ ligands and the very polar solvent $MeNO_2$ controls the identity of the obtained crystalline product. The reaction solutions are likely complicated equilibria of several species; the exact equilibrium composition and the identity of the product that crystallizes thus reasonably depend on the charge of the species, solvent polarity, ligand hydrophobicity, *etc.*

X-Ray analysis§ of complex **2**·$pdmH_2$ (Fig. 1) reveals a structure that is distinctly different from that of any previously structurally characterised octanuclear Mn complex.[9] The structure contains a $[Mn^{II}_6Mn^{III}_2(\mu_4\text{-}O)_2(\mu_2\text{-}O)_8]^{2-}$ core (Fig. 2a), which can be considered as an extension of the $[Mn_6O_6]^{2+}$ core of **3** (Fig. 2b). In the hexanuclear species, the six O atoms of the core consist of two μ_2-O^{2-} ions and four μ_2-O atoms from carboxylate ligands. This unit is exactly reproduced in **2** and comprises Mn(1–6) and O(9,10,43,53,61,67). Extension of this hexanuclear core at one end with two additional Mn atoms, Mn(7) and Mn(8), each with a bis(μ_2-O(carboxylate)) bridge to Mn(6) and Mn(5), respectively, affords the octanuclear core of complex **2**. Bond valence sum calculations indicate that Mn(3) and Mn(4) are Mn^{III}, while the remaining Mn centers are Mn^{II}. In addition, Mn(3) and Mn(4) display Jahn-Teller (JT) elongation, typical of high spin Mn^{III} (d^4), with the JT axes avoiding the bridging oxide ions and instead oriented along O(43)–Mn(3)–O(61) and O(53)–Mn(4)–O(67). This is an identical arrangement to that observed in **3**. Furthermore, although there is no crystallographic symmetry, the core possesses a virtual C_2 axis, passing through O(9) and O(10). The peripheral ligation for complex **2** is provided by fourteen $Bu^tCH_2CO_2^-$ and four $Bu^tCH_2CO_2H$ ligands. The four $Bu^tCH_2CO_2H$ ligands all bind in a monodentate fashion, with the 'dangling' OH fragments

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displaying strong intramolecular OH···O hydrogen bonds to O atoms from four of the $Bu^tCH_2CO_2^-$ ligands, with O···O separations varying from 2.53 to 2.64 Å.

Variable temperature dc susceptibility measurements were performed on a microcrystalline sample of **2** in a 10 kG field in the range 1.8–300 K (Fig. 3). The $\chi_M T$ value of 24.8 $cm^3 mol^{-1}$ K at 300 K decreases gradually as the temperature is decreased to 0.9 cm^3 K mol^{-1} at 1.8 K. The spin-only ($g = 2$) value for a unit composed of non-interacting $Mn^{II}_6Mn^{III}_2$ is 32.2 cm^3 K mol^{-1}, suggesting appreciable antiferromagnetic interactions in **2**. In order to investigate this further, ac susceptibility measurements were performed in the range 1.8–30 K with a 3.5 G ac field oscillating at 997 Hz. The ac data (not shown) are essentially superimposable with the dc data and appear to be heading for $\chi_M T = 0$ cm^3 K mol^{-1} at 0 K. Thus, both sets of data are consistent with an $S = 0$ ground state. This can be rationalized by considering the structural relationship between **2** and **3**. In complex **3**, the dominant exchange interaction is the antiferromagnetic one ($J = -42$ cm^{-1}) between the Mn^{III} centers, which results in an overall $S = 0$ ground state whatever the spins of each of the two halves of the molecule might be.[3] The core of complex **3** is essentially preserved in **2**, which differs only by the presence of two additional peripheral Mn^{II} centres. Hence, the dominant exchange interaction is again likely to be an antiferromagnetic one between Mn(3) and Mn(4), resulting in the observed $S = 0$ ground state for the complex.

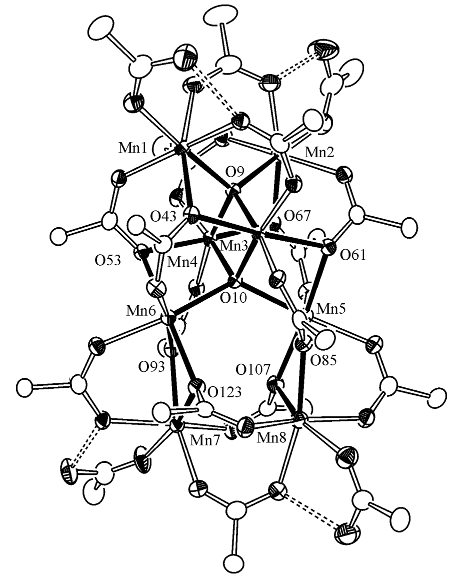

Fig. 1 ORTEP representation of complex **2** at the 50% probability level. For clarity, only the methylene C atoms of the ligands are shown. Selected interatomic distances (Å) are: Mn(1)···Mn(2) 3.707(2), Mn(1)···Mn(3) 3.171(2), Mn(1)···Mn(4) 3.509(2), Mn(2)···Mn(3) 3.500(2), Mn(2)···Mn(4) 3.138(2), Mn(3)···Mn(4) 2.800(2), Mn(3)···Mn(5) 3.217(2), Mn(3)···Mn(6) 3.479(2) Mn(4)···Mn(5) 3.566(2), Mn(4)···Mn(6) 3.152(2), Mn(5)···Mn(8) 3.316(2), Mn(6)···Mn(7) 3.359(2).

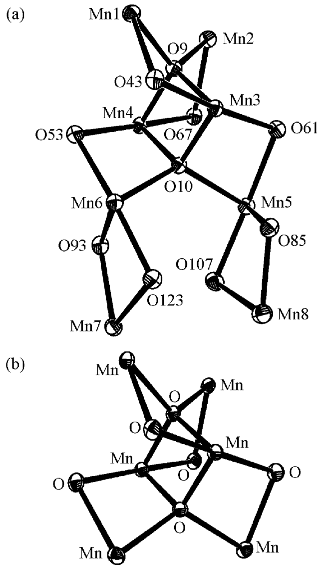

Fig. 2 ORTEP representation of the cores of (a) complex **2** and (b) complex **3** at the 50% probability level.

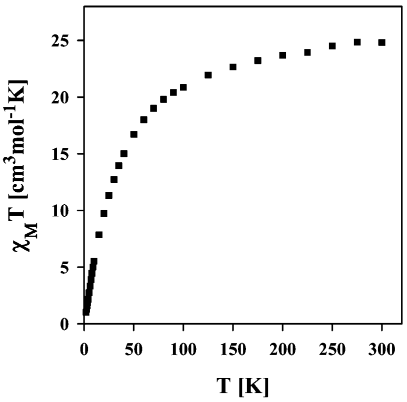

Fig. 3 Plot of $\chi_M T$ *vs* T for complex **2** measured in a 10 kG field.

In conclusion, we have described that reductive activation of a large $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ cluster leads to a nuclearity decrease and a new octanuclear Mn carboxylate cluster (**2**) not obtained from previous methodology. The synthesis of **2** involves the reduction of a member of the large Mn_{12} family of complexes, and represents a new and potentially widely applicable route to new Mn_x clusters. Work is in progress to further exploit both the reductive activation of large Mn_{12} (and other) clusters, and the ability of the ligand/solvent combination to vary the identity of the obtained product, particularly given the wide variety of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ with different carboxylate groups currently known.

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Notes and references

‡ The vacuum-dried material analysed as unsolvated. Found: C, 50.98; H, 8.01; N, 0.00. Calc. for $C_{108}H_{202}Mn_8O_{38}$: C, 50.90; H, 7.99; N, 0.00%.

§ *Crystal data* for $2 \cdot pdmH_2$, $C_{115}H_{211}Mn_8NO_{40}$, $M_r = 2687.43$, triclinic, space group $P1$, $a = 14.7812(4)$, $b = 15.0833(4)$, $c = 35.2358(9)$ Å, $\alpha = 78.735(1)$, $\beta = 84.815(1)$, $\gamma = 61.914(1)°$, $U = 6797.18$ Å^3, $Z = 2$, $T = -156$ °C, μ(Mo-Kα) = 7.923 cm^{-1}. Residuals were $R = 0.044$, $R_w = 0.044$ from refinement on F using 20140 unique data with $F > 2.33\sigma(F)$. CCDC 189990. See http://www.rsc.org/suppdata/cc/b2/b206751j/ for crystallographic data in CIF or other electronic format.

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