A novel octanuclear Mn(III) aggregate as a single-molecule magnet†

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The novel octanuclear cluster [Mn$_8$O$_2$(OH)$_2$(OMe)$_{12}$(OAc)$_2$-(Mesalim)$_4$] (1) presents SMM behaviour with a relatively high experimental energy barrier (Δ_{eff}/k_B = 36.0 K) as shown by its dc and ac magnetic properties.

The ability of a molecule to act as a nano-magnet is of potential interest for future data-storage applications. Such a molecule, commonly named a single-molecule magnet (SMM),[1,2] displays slow relaxation of its magnetization and functions as a magnet below its blocking temperature (T_B). The relaxation time of the magnetization, τ, is thermally activated and results mainly from the spin ground state (S_T) and the uni-axial anisotropy (D) of the molecule. In this regime, the theoretical energy barrier Δ is equal to $|D|\ S_T^2$ or $|D|\ (S_T^2 - 1/4)$ for integer and half-integer S_T, respectively. Although many efforts have been made to increase Δ and thus T_B, the first family of SMMs, [Mn$_{12}$O$_{12}$(OR)$_{12}$(H$_2$O)$_4$], still displays so far the highest blocking temperatures.[1,2] Synthetic strategies in this field of research mostly rely on obtaining cores of transition metal ions with a high-spin ground state and a high single-ion anisotropy, using for example Mn(III) or Fe(III) linked through oxo- and/or carboxylato groups.[3,4] Organic chelating ligands, which can act as an outer shell to these cores, are efficient in varying core size and key structural parameters such as Jahn–Teller (JT) elongation axis orientations (thus D), and the magnetic interaction scheme (thus S_T).[5] We have been using HMesalim (see Scheme 1) as a chelating ligand for studying the manganese and iron complexes in oxidation catalysis and report here on the structure and properties of [Mn$_8$O$_2$(OH)$_2$(OMe)$_{12}$(OAc)$_2$-(Mesalim)$_4$] (1), which is the first compound of this ligand to behave as an SMM.

The reaction of HMesalim with manganese(II) acetate in a 2 : 1 ratio in a methanol–ether mixture yields the mononuclear complex [Mn(Mesalim)$_2$(OAc)(MeOH)]·MeOH (2), the crystal structure of
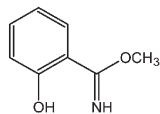
Scheme 1   The ligand HMesalim (methyl salicylimidate).

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which has recently been reported.[6] The octanuclear complex 1 was obtained as brown crystals by very slow evaporation of a dilute methanol solution of 2 over a period of three months.‡ Despite the low yields and longer times necessary for the crystallisation, the complex can be readily reproduced. Structural analysis§ shows the compound to consist of neutral octanuclear clusters (see Fig. 1), containing eight Mn(III) metal ions, two μ_4-O^{2-}, two μ_3-OH$^-$, ten μ-OMe$^-$, two terminal OMe$^-$, two OAc$^-$ anions and four terminal anionic Mesalim ligands. An alternative description of the complex would involve two terminal MeOH instead of OMe$^-$ and two O^{2-} instead of OH$^-$. These descriptions differ only in the position of two H atoms. These H atoms are most likely disordered and could not be located on difference Fourier maps. The molecule has non-crystallographic inversion symmetry (RMS deviation 0.109 Å). All manganese ions are in a pseudo-octahedral environment. The four peripheral ones (Mn1, Mn4, Mn7 and Mn8) are in an NO$_5$ coordination sphere, whereas the four central manganese ions (Mn2, Mn3, Mn5 and Mn6) have MnO$_6$ chromophores. Complex 1 can be described as consisting of six [Mn$_3$O$_4$] partial cubane units that are commonly encountered in high nuclearity manganese compounds, the two central units sharing one face. Furthermore, each of the central partial cubane units shares a face with two of the four remaining units. The two terminal MeO$^-$ ions, the bridging acetates and the anionic
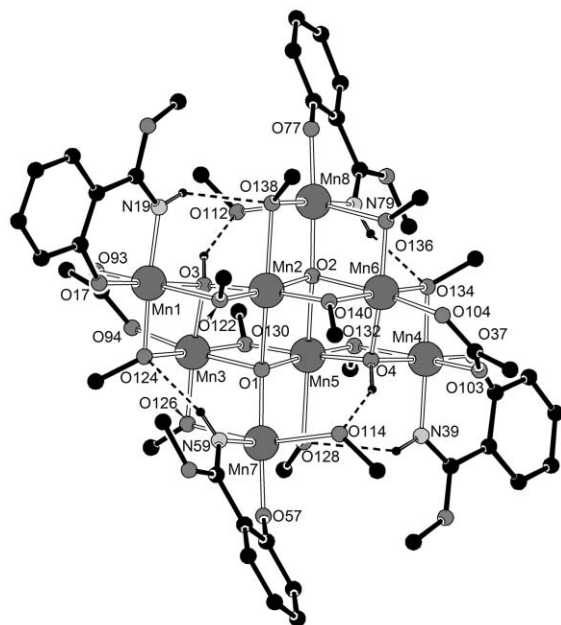

Fig. 1   A PLUTON view of the structure of complex 1. H atoms not participating in H-bonds (dashed lines) are omitted for clarity.

Mesalim ligands are not involved in the formation of partial cubanes, and complete the coordination sphere around the manganese ions. Pairs of neighbouring manganese ions are connected by two O bridges, the exception being the Mn1–Mn3 pair, and its pseudo-symmetrical counterpart Mn4–Mn6 pair, which have an additional acetate bridge resulting in shorter Mn⋯Mn separation (2.94 Å). In addition, the Mn2–Mn7 and Mn5–Mn8 pairs are connected by a single unique asymmetric μ_4-O^{2-} bridge (for the Mn2–Mn7 pair: Mn–O = 2.295(5) and 1.911(5) Å, Mn–O–Mn = 150.7(3)°, for Mn5–M8: Mn–O = 2.305(5) and 1.921(5) Å, Mn–O–Mn = 150.8(3)°) resulting in a longer Mn⋯Mn separation (4.070(2) Å). All Mn(III) ions present elongated JT axes, which is known to result in a negative value of the axial zero field splitting parameter.[7] In the central Mn2–Mn5 pair both bridging O atoms lie along the JT elongation axis of either of the Mn ions, the JT axes of the two Mn(III) ions being parallel with each other in this case (Fig. 2) (short Mn–O bond, 1.957(6) and 1.967(6) Å, long Mn–O bond, 2.295(5) and 2.305(5) Å, Mn2⋯Mn5 = 3.248(2) Å). In contrast, in the rest of the pairs (Mn⋯Mn separations of 3.02 to 3.09 Å) only one of the two bridging O atoms lies on the JT axis of one of the manganese ions resulting in the orthogonality of the JT axes. The JT axes of Mn1, Mn4, Mn7 and Mn8 are all parallel to each other; the JT axis of Mn2 is parallel to Mn5 while the JT axis of Mn3 is parallel to Mn6. Each of the above three groups of parallel JT axes are approximately orthogonal to the other two orientations. A resulting significant magnetic anisotropy can thus be expected. Remarkably, the outer manganese ions do not have their JT axes along the bonds to ligand oxygen or nitrogen atoms. It is worth noting that octanuclearity in purely Mn(III) oxo/carboxylato compounds is still rather rare,[8] and the core present in **1** has not been reported so far. However, the central Mn$_6$ core resembles that of a hexamanganese complex reported by Tuchagues *et al.*[9]

Results of dc magnetic susceptibility measurements on a polycrystalline sample of **1** are depicted in Fig. 3. The $\chi_M T$ product increases from 24.2 cm³ K mol⁻¹ at 300 K to reach a maximum of 108.3 cm³ K mol⁻¹ at 6.7 K, and then decreases to 78.4 cm³ K mol⁻¹ at 1.83 K. This behaviour indicates the presence of dominant ferromagnetic interactions among the [Mn$_8$] core, yielding a high-spin ground state. The value of $\chi_M T$ at 300 K is
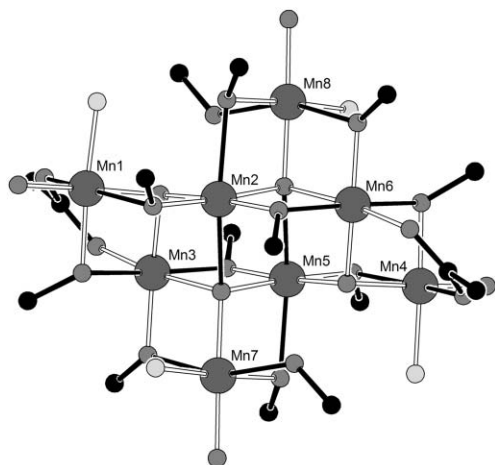

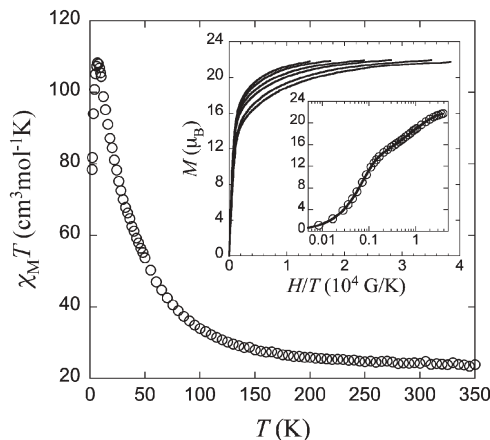**Fig. 2** A PLUTON view of the core of complex **1**. JT axes of all Mn(III) ions are emphasized in black.

Fig. 3 Plot of $\chi_M T$ *vs.* *T* at 0.1 T. Inset: Reduced magnetization data as normal and semilog plots.

in good agreement with the spin only value for eight uncoupled $S = 2$ spins, *e.g.* 24 cm³ K mol⁻¹. Owing to the size of the molecule and the symmetry of the interaction scheme, it was neither possible to apply the Kambe method[10] nor a simple numerical approach to evaluate the exchange parameters between the Mn(III) ions. Nevertheless, the central Mn2–Mn5 interaction is expected to be ferromagnetic, as observed in such out-of-plane Mn(III) dimeric units,[11] while the other exchange parameters are likely to be much weaker, of either sign. The reduced magnetization plot presents a very steep increase of M at low fields up to a value of *ca.* 16 μ_B (in agreement with a $S_T = 8$ ground state), and then a slower increase, without reaching saturation at the highest field (7 T). This feature and the lack of low temperature saturation of the $\chi_M T$ product (see the semilog $\chi_M T$ *vs.* *T* plot in supplementary data, Fig. S1†) indicate that even at the experimental lowest temperature low-lying excited states are populated. Moreover, the fact that the data are not superimposed clearly indicates the presence of magnetic anisotropy (zero field splitting, ZFS). This behaviour could not be reproduced by considering that only the ground state is populated at the temperatures studied (1.83–4 K), as is usually done to ascertain the value of the spin ground state and its anisotropy parameter D.[12] Hence the most probable situation is that the spin ground state of complex **1** would be $S_T = 8$, but with very low-lying excited spin-states. An $S_T = 8$ ground state would be in agreement with a central Mn2–Mn5 ferromagnetic interaction, the rest of the Mn pairs being antiferromagnetically coupled. The fall of $\chi_M T$ at low temperatures is then either a consequence of intramolecular competing antiferromagnetic and ferromagnetic interactions among these pairs (note that no significant inter-molecular interactions have been observed in the crystal structure) and/or of magnetic anisotropy (ZFS).

Slow relaxation of the magnetization was studied using ac techniques. The frequency dependence of the ac susceptibility on a polycrystalline sample of **1** was measured at different temperatures down to 1.83 K under zero applied dc field (Fig. 4). As expected for a SMM, the ac susceptibility and especially its out-of-phase component are strongly frequency-dependent indicative of a slow magnetization-relaxation phenomenon. Remarkably, blocking temperatures can be observed in **1** at reasonable temperatures, *i.e.* above 3 K for frequencies higher than 500 Hz. Fig. 4 as well as
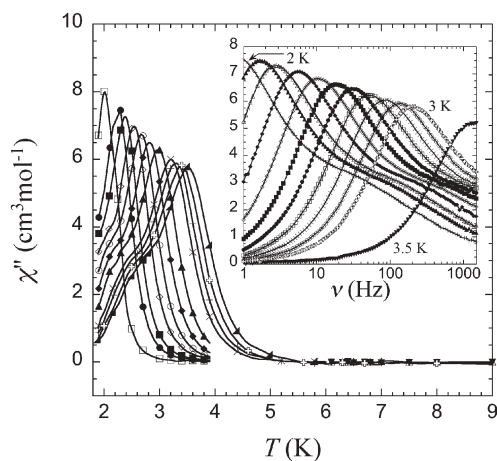
Fig. 4 Plot of χ'' vs. T at 0 T dc field (frequencies from left to right: 1, 5, 10, 25, 50, 100, 199, 498, 699, 997 and 1488 Hz). Inset: Plot of χ'' vs. ν at 0 T dc field at temperatures between 2 and 3 K and at 3.5 K.

Cole–Cole plots (see supplementary material, Fig. S2†) indicate the presence of a second relaxation mode at higher frequencies, aside from the main one observed, which could be due to a small impurity or to intermolecular effects.[13] From the data in Fig. 4, the main relaxation time τ can be determined from the maximum of χ'' as a function of both temperature and frequency. In the temperature domain studied the relaxation time follows the Arrhénius law with $\Delta/k_B = 36.0$ K and $\tau_0 = 4.39 \times 10^{-9}$ s (for $T > 2.1$ K, see Fig. 5), indicating that the relaxation is thermally activated. As in many SMMs, it is likely that Δ corresponds in fact to an effective barrier, resulting from the short-cut of the thermal barrier by quantum tunnelling of magnetization. In **1**, the experimental energy barrier $\Delta_{eff}/k_B = 36.0$ K remains relatively large. The octanuclear core of **1** is thus a new addition to the still quite small number of metal ion cores in which this behaviour has been observed at reasonably high temperatures.

In summary, a novel octanuclear Mn(III) SMM cluster has been isolated with the ligand HMesalim, which thus represents an interesting new entry in the small list of chelating ligands used so far in this field. The study of the magnetic properties of the novel cluster has revealed a rather high-energy barrier allowing the observation of thermally activated relaxation above 3 K.
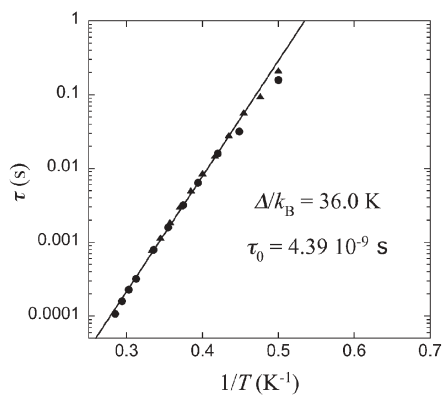

Fig. 5 Plot of τ vs. T^{-1} determined by ac measurements (full circles: temperature data, full triangles: frequency data). The solid line represents the Arrhenius fit.

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