

Magnetothermal Studies of a Series of Coordination Clusters Built from Ferromagnetically Coupled $\{\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_6\}$ Supertetrahedral Units

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Abstract: Three high-nuclearity mixed valence manganese^{II/III} coordination clusters, have been synthesised, that is, $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4(\mu_3\text{-O})_4(\text{HL}^1)_6(\mu_3\text{-N}_3)_3(\mu_3\text{-Br})(\text{Br})](\text{N}_3)_{0.7}/(\text{Br})_{0.3}\cdot 3\text{MeCN}\cdot 2\text{MeOH}$ (**1**) ($\text{H}_3\text{L}^1 = 3\text{-methylpentan-1,3,5-triol}$), $[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}_6(\mu_4\text{-O})_8(\mu_3\text{-Cl})_4(\mu_4, \mu_3\text{-O}_2\text{CMe})_2(\mu_4, \mu\text{-L}^2)_{10}\text{Cl}_{2.34}(\text{O}_2\text{CMe})_{0.66}\text{-}(\text{py})_3(\text{MeCN})_2]\cdot 7\text{MeCN}$ (**2**) ($\text{H}_2\text{L}^2 = 2,2\text{-dimethyl-1,3-propanediol}$ and py is pyridine), and $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8(\mu_3\text{-}\eta^1\text{N}_3)_8(\text{HL}^3)_{12}(\text{MeCN})_6]\text{Cl}_2\cdot 10\text{MeOH}\cdot \text{MeCN}$ (**3**) ($\text{H}_3\text{L}^3 = 2,6\text{-bis(hydroxymethyl)-4-methylphenol}$) with high ground-spin states, $S = 22$, 28 ± 1 , and $83/2$, respectively; their magnetothermal properties have been studied. The

three compounds are based on a common supertetrahedral building block as seen in the Mn_{10} cluster. This fundamental magnetic unit is made up of a tetrahedron of Mn^{II} ions with six Mn^{III} ions placed midway along each edge giving an inscribed octahedron. Thus, the fundamental building unit as represented by compound **1** can be described as a Mn_{10} supertetrahedron. Compounds **2** and **3** correspond to two

such units joined by a common edge or vertex, respectively, resulting in Mn_{17} and Mn_{19} coordination clusters. Magnetothermal studies reveal that all three compounds show interesting long-range magnetic ordering at low temperature, originating from negligible magnetic anisotropy of the compounds; compound **2** shows the largest magnetocaloric effect among the three compounds. This is as expected and can be attributed to the presence of a small magnetic anisotropy, and low-lying excited states in compound **2**.

Keywords: cluster compounds • magnetic properties • magnetocaloric effects • manganese • polynuclear complexes

Introduction

The synthesis and investigation of high nuclearity metal complexes, which can be described as coordination clusters, have opened up an extremely active area in inorganic

chemistry over the last couple of decades.^[1–3] Initially, the principal interest in producing clusters of transition-metal ions arose through the attempts of biomimetic coordination chemists to mimic the active sites of the increasing number of metalloenzymes identified. In particular, the mystery with which the oxygen evolving centre of Photosystem II of the photosynthetic apparatus, based on a tetranuclear collection of manganese ions, was (and largely still is) shrouded, serving to push efforts in a whole new area of manganese coordination cluster chemistry.^[4,5] This impetus, in association with the desire to try to shed light on the electronic states important through the catalytic cycle,^[6] led to the discovery that incorporation of the Mn^{III} ion into such clusters could induce slow relaxation of the magnetisation.^[2,7,8] This opened up a completely new field of interest in producing compounds with high ground-spin states and magnetic anisotropy, which need to be combined, with the promise of applications in magnetic data storage, processing and molecular spintronics.^[7,9] However, it has since been acknowledged that achieving the optimum combination of spin and anisotropy is far from straightforward and although examples have been found with improved values, compared with the

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201001988>.

original Mn_{12}Ac example, for both the uniaxial anisotropy parameter D and spin value S_z , these have not so far been combined within one and the same molecule.^[10] In fact, it seems that the higher the ground-spin state in a molecule becomes, the lower the overall anisotropy becomes, with the result that the manganese coordination clusters stabilising high spins have low, if not negligible D values. However, it was soon realised that there could be an enormous benefit to having high spin molecules with minimal anisotropy, since these could be used for magnetic refrigeration.^[11–14]

The concept of magnetic refrigeration is based on the magnetocaloric effect, hereafter MCE. Briefly it can be defined as the magnetic entropy change, and related adiabatic temperature change, due to varying magnetic field. The principle can be easily explained by the entropy (S) versus temperature (T) plot, as shown in Figure 1. In the presence

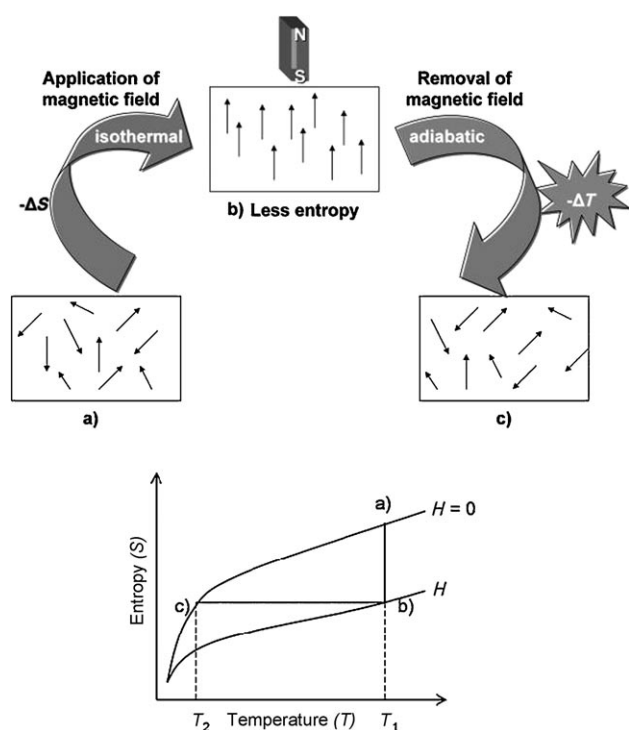


Figure 1. Schematic diagram explaining the magnetocaloric effects (MCE).

of a magnetic field, the entropy of a magnetic substance decreases due to spin alignment. Let us consider a substance at point “a”, at which the magnetic field is zero on the plot, that is then isothermally magnetised to the point “b” by applying a magnetic field H . If the magnetic field is then removed ($H=0$) adiabatically, the substance will go to point “c”, causing a decrease in temperature ($T_2 < T_1$). The effect can also be presented using the thermodynamic relationship given in Equation (1), in which C_H and M stand for heat capacity and magnetisation, respectively.^[15] In case of an isothermal process, $dT=0$, and we can derive Equation (2).

$$Tds = C_H dT + T \left(\frac{dM}{dT} \right)_H dH \quad (1)$$

$$Tds = T \left(\frac{dM}{dT} \right)_H dH \quad (2)$$

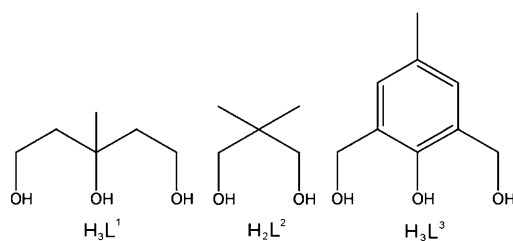
According to the Curie law $\chi = C/T$, we obtain the magnetisation $M = \chi H = CH/T$, and thus $(dM/dT)_H$ becomes negative and therefore dS becomes negative at the first step. At the second step, since the process is adiabatic, that is, $dS=0$ and from Equation (1), dT is negative and therefore the system cools down. Possible applications of this effect include the ability to cool down at a molecular level, at very low temperature beyond the reach of liquid helium.

For such a case, the requirement becomes to find molecules with high ground-spin states and low anisotropy and clear candidates are the variations on coordination clusters that can be recognised as being built up from a basic supertetrahedral unit, in which a tetrahedron of four Mn^{II} ions has an octahedron of six Mn^{III} ions inscribed within it so that each Mn^{III} is placed midway along each edge of the tetrahedron. This motif is apparently comparatively stable and has been observed in an isolated form by a number of groups; we first observed it as the building block of a Mn_{19} coordination cluster, in which two such supertetrahedra are joined by a common vertex, and subsequently in a Mn_{17} compound, in which the supertetrahedra share a common edge. Other groups have also reported compounds in which this $\{\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_6\}$ motif occurs, although it has not always been recognised as such. In all cases the supertetrahedral Mn_{10} units display ferromagnetic cooperative coupling, but vanishing anisotropy as a result of the octahedral arrangement of the Mn^{III} centres.^[3,4,13,14,16]

We therefore decided to study the magnetocaloric properties in detail of the three high-spin manganese clusters $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4(\mu_3\text{-O})_4(\text{HL}^1)_6(\mu_3\text{-N}_3)_3(\mu_3\text{-Br})(\text{Br})](\text{N}_3)_{0.7}(\text{Br})_{0.3} \cdot 3\text{MeCN} \cdot 2\text{MeOH}$ (**1**, $S=22$), $[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}_6(\mu_4\text{-O})_8(\mu_3\text{-Cl})_4(\mu_3\mu_3\text{-O}_2\text{CMe})_2(\mu_3\mu\text{-L}^2)_{10}\text{Cl}_{2.34}(\text{O}_2\text{CMe})_{0.66}(\text{py})_3(\text{MeCN})_2] \cdot 7\text{MeCN}$ (**2**, $S=28 \pm 1$), and $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8(\mu_3\text{-}\eta^1\text{N}_3)_8(\text{HL}^3)_{12}(\text{MeCN})_6]\text{Cl}_2 \cdot 10\text{MeOH} \cdot \text{MeCN}$ (**3**; with the record ground-spin state of $S=83/2$).^[17,18]

Results and Discussion

Synthetic strategy: The syntheses of all the compounds used in this study have been previously reported by some of us elsewhere.^[17–19] Nevertheless, it is worth pointing out here the overall strategy that we have used to obtain these high-spin molecules based on the supertetrahedron motif. It was pointed out many years ago that ligands incorporating alcohol arms are useful for bridging between metal centres,^[20] and more recently polyol ligands have received increasing attention as a means for assembling transition metals into high-nuclearity complexes.^[21] Keeping their versatile potential in mind, polyalcohol-based ligands (shown here) were used in our synthesis. Moreover, azide and acetate were



used as co-ligands, because of their different kinds of coordination modes that often facilitate the formation of polynuclear transition-metal complexes with interesting magnetic coupling.^[13,17,18] A trialcohol ligand, 3-methyl pentane-1,3,5-triol (H_3L^1), was used together with sodium azide and manganese(II) bromide tetrahydrate and sodium acetate to synthesise compound **1**, $[Mn^{III}_6Mn^{II}_4(\mu_3-O)_4(HL_1)_6(\mu_3-N_3)_3(\mu_3-Br)(Br)](N_3)_{0.7}(Br)_{0.3} \cdot 3 MeCN \cdot 2 MeOH$.^[19]

A dialcohol ligand, 2,2-dimethyl-1,3-propanediol (H_2L^2), together with pyridine and sodium acetate was used to synthesise compound **2**, $[Mn^{III}_{11}Mn^{II}_6(\mu_4-O)_8(\mu_3-Cl)_4(\mu_3, \mu_3-O_2CMe)_2(\mu_3, \mu-L^2)_{10}Cl_{2.34}(O_2CMe)_{0.66}(py)_3(MeCN)_2] \cdot 7 MeCN$, and a trialcohol ligand 2,6-bis(hydroxy-methyl)-4-methylphenol (H_3L^3) was used together with manganese chloride, sodium azide, and sodium acetate to synthesise compound **3**, $[Mn^{III}_{12}Mn^{II}_7(\mu_4-O)_8(\mu_3, \eta^1-N_3)_8(HL^3)_{12}(MeCN)_6]Cl_2 \cdot 10 MeOH \cdot MeCN$.

Structural description: The molecular motifs of compounds **1**, **2** and **3**, as established from the single-crystal X-ray analyses,^[17–19] are shown in Figure 2 (some of the most relevant crystallographic data are given in Table 1). In all the complexes there are manganese ions in the 2+ and 3+ oxidation states as established by bond-valence sum (BVS) analysis and by considering the presence of Jahn–Teller (JT) axes along Mn^{III} centres.^[17,18] It can be seen that

in compound **1**, the manganese ions are held together by the presence of bridging oxido, azido (end-on mode) and bromido groups. In case of compound **2**, the bridging ligands are oxido, chlorido and acetato. However, in compound **3**, the manganese ions are held together by the bridging oxido and azido (end-on mode) groups only. The cores of the three compounds are geometrically very closely related as can be seen in Figure 3. There is a wide range of M–O–M bond angles. For example, in compound **1**, the M–O–M bond angles are between 100.96

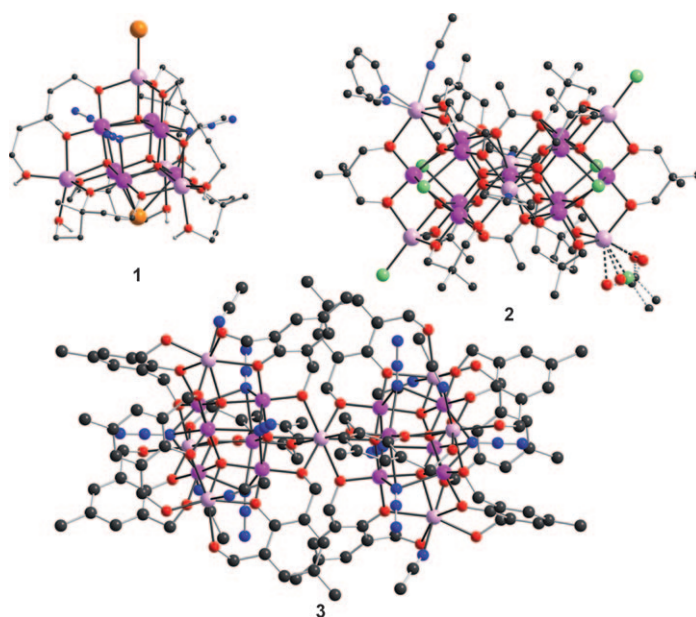


Figure 2. Crystallographic views of compounds **1**, **2**, and **3**. Colour codes for atoms are: blue (N), dark grey (C), green (Cl), dark pink (Mn^{III}), light pink (Mn^{II}), red (O), and dark yellow (Br). Two disordered acetate groups are shown with broken-off bonds in **2**.

Table 1. Relevant crystal structure parameters of compound **1**, **2**, and **3**.^[a]

	1	2	3
formula	$C_{44}H_{89}Br_{2.70}Mn_{10}N_{12.90}O_{24}$	$C_{88.32}H_{149.98}Cl_{6.34}Mn_{17}N_{12}O_{33.32}$	$C_{132}H_{181}Cl_2Mn_{19}N_{31}O_{54}$
M_r	1948.04	3071.88	4180.84
crystal system	trigonal	triclinic	trigonal
space group	$R\bar{3}$	$P\bar{1}$	$R\bar{3}$
a [Å]	13.4560(3)	15.1766(6)	20.9989(6)
b [Å]	13.4560(3)	16.6851(7)	20.9989(6)
c [Å]	35.2135(14)	26.4026(11)	34.7489(14)
α [°]	90.00	97.2440(10)	90.00
β [°]	90.00	100.9490(10)	90.00
γ [°]	120.00	105.0310(10)	120.00
V [Å ³]	5521.7(3)	6230.1(4)	13269.8(8)
Z	3	2	3
ρ_{calc} [g cm ⁻³]	1.758	1.638	1.570
$\mu(MoK\alpha)$ [mm ⁻¹]	3.194	1.864	1.418
$F(000)$	2939	3126	6393
R_{int}	0.0177	0.0271	0.0253
reflns obsd [$I > 2\sigma(I)$]	5154	18659	4991
parameters/restraints	309/58	1428/119	382/17
GOF on F^2	1.053	1.085	1.036
$R1$ [$I > 2\sigma(I)$]	0.0381	0.0588	0.0414
$wR2$ (all data)	0.1030	0.1311	0.1218

[a] CCDC-775349 (**1**), 703713 (**2**) and 604216 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

and 102.90°. In compound **2**, this range is broader and the angles fall in the range between 98.51 and 116.68°. In compound **3**, these angles fall in the range between 101.08 and 114.26°. There are μ_3 -Br and μ_3 -Cl groups present in compounds **1** and **2**, respectively. The M–Br–M, and M–Cl–M angles fall in the range between 71.56–71.57° and 73.34–76.17°, respectively. These small angles probably play an im-

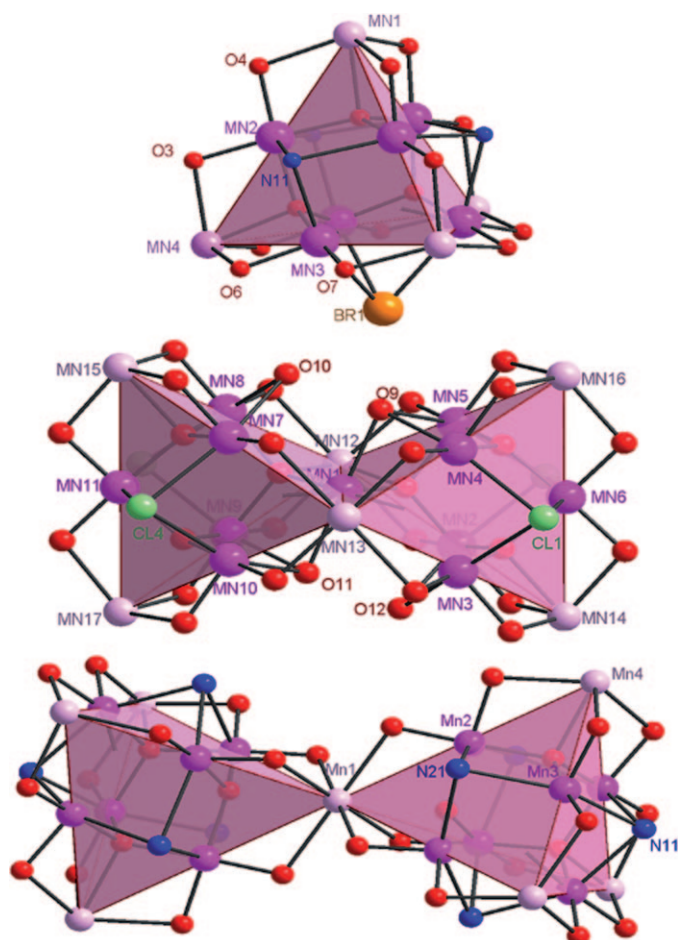


Figure 3. Polyhedral representation of the manganese core of compound **1**, **2**, and **3** (top, middle and bottom, respectively). Only the metal ions and the bridging atoms are shown for clarity. Colour code for atoms: blue (N), green (Cl), dark pink (Mn^{III}), light pink (Mn^{II}), red (O), and dark yellow (Br).

portant role in ferromagnetic coupling between the bridged metal ions. The end-on azido bridging is also very important for these kinds of compounds, because of their small M-N-M angles which facilitate orthogonal overlapping of the orbitals and thus ferromagnetic coupling.^[22] These angles fall in the ranges 84.48–86.62 and 80.29–84.75° in compounds **1** and **3**, respectively. As mentioned above, all the compounds have supertetrahedral building units. Compound **1** has the isolated unit made up of four Mn^{II} ions at the vertices of the tetrahedral motif (Figure 3) and six Mn^{III} ions, each sitting at the centre of the six edges of the tetrahedron. Compound **2** has seventeen manganese ions that describe two tetrahedra sharing a common edge, with the same arrangement of Mn^{II} and the Mn^{III} ions as for **1**; that is, the six Mn^{II} ions are sitting at the six vertices of the two fused tetrahedra, whereas the eleven Mn^{III} ions are located at the centres of the eleven edges of the two fused tetrahedra (Figure 3). In compound **3**, two supertetrahedral unit share a common vertex, so there are seven Mn^{II} ions at the vertices of the fused tetrahedral and twelve Mn^{III} ions at the centres of their edges

(Figure 3). A common feature of coordination behaviour of the polyalkoxy ligands in all three complexes is that, in spite of their different structures and different numbers of hydroxyl groups, they coordinate to the three manganese ions describing the edges of the supertetrahedra (Figure 2).

Magnetic and magnetocaloric studies: Magnetic properties of all the complexes were studied before in detail.^[17–19] The magnetic properties of the three compounds are briefly summarised below.

$[Mn^{III}_6Mn^{II}_4(\mu_3-O)_4(HL^1)_6(\mu_3-N_3)_3(\mu_3-Br)(Br)](N_3)_{0.7}(Br)_{0.3} \cdot 3MeCN \cdot 2MeOH$ (**1**): The room-temperature value of the magnetic susceptibility and temperature product χT of 51.1 emu K mol⁻¹ for **1** is higher than the expected value of 35.5 emu K mol⁻¹ ($g=2$) for four Mn^{II} ($S=5/2$) and six Mn^{III} ($S=2$) ions, indicating dominating ferromagnetic interactions between the manganese ions (Figure 4a). With decreasing temperature χT increases up to a maximum of 216.6 emu K mol⁻¹ at 6 K. This is also consistent with ferromagnetic coupling between the Mn ions with the maximum value at 6 K, in line with the expected value of 216.5 emu K mol⁻¹ for an $S_T=22$ ground state with $g=1.85$. The M versus H plot indicates that the magnetisation saturates at 40.8 μ_B , which is also what would be predicted for an $S_T=22$ ground state with $g=1.85$ (this is reasonable for compounds containing Mn^{III} ions). The M versus H/T plots at different temperatures are almost superposed (Figure S1 in the Supporting Information), suggesting the lack of magnetic anisotropy in the complex. The lack of anisotropy is most likely due to the highly symmetric structure which facilitates to cancel out the anisotropy contributions mainly from JT distortions of the Mn^{III} ions. A similar compound with different ligand has been reported in the recent past by Brechin et al.^[14]

$[Mn^{III}_{11}Mn^{II}_6(\mu_4-O)_8(\mu_3-Cl)_4(\mu_3-O_2CMe)_2(\mu_3-L^2)_{10}Cl_{2,34} \cdot (O_2CMe)_{0.66}(py)_{3-} \cdot (MeCN)_2] \cdot 7MeCN$ (**2**): The room-temperature value of the magnetic susceptibility and temperature product χT of 61.0 cm³ K mol⁻¹ (Figure 4c) is slightly higher than the expected value of 59.25 cm³ K mol⁻¹ for six Mn^{II} and eleven Mn^{III} ions, indicating dominating ferromagnetic interactions between the manganese ions. The decrease of the χT product below 11 K suggests that additional effects, such as intermolecular antiferromagnetic interactions, are present between the cluster units. The magnetisation increases rapidly at higher magnetic fields and reaches almost 58 μ_B at saturation, leaving a slight slope that suggests the presence of small magnetic anisotropy. Considering the near-saturation of the magnetisation at 58 μ_B , a ground-state spin of $S_T=29$ can be proposed ($g=2$). This value can be rationalised by a situation in which the spins of two Mn^{III} ions are antiparallel to the rest of the Mn^{II} and the nine Mn^{III} ions. Extrapolating the χT value to very low temperatures, at which only the ground state would be expected to be populated, provides an experimental value close to 400 cm³ K mol⁻¹. This in turn suggests a slightly lower

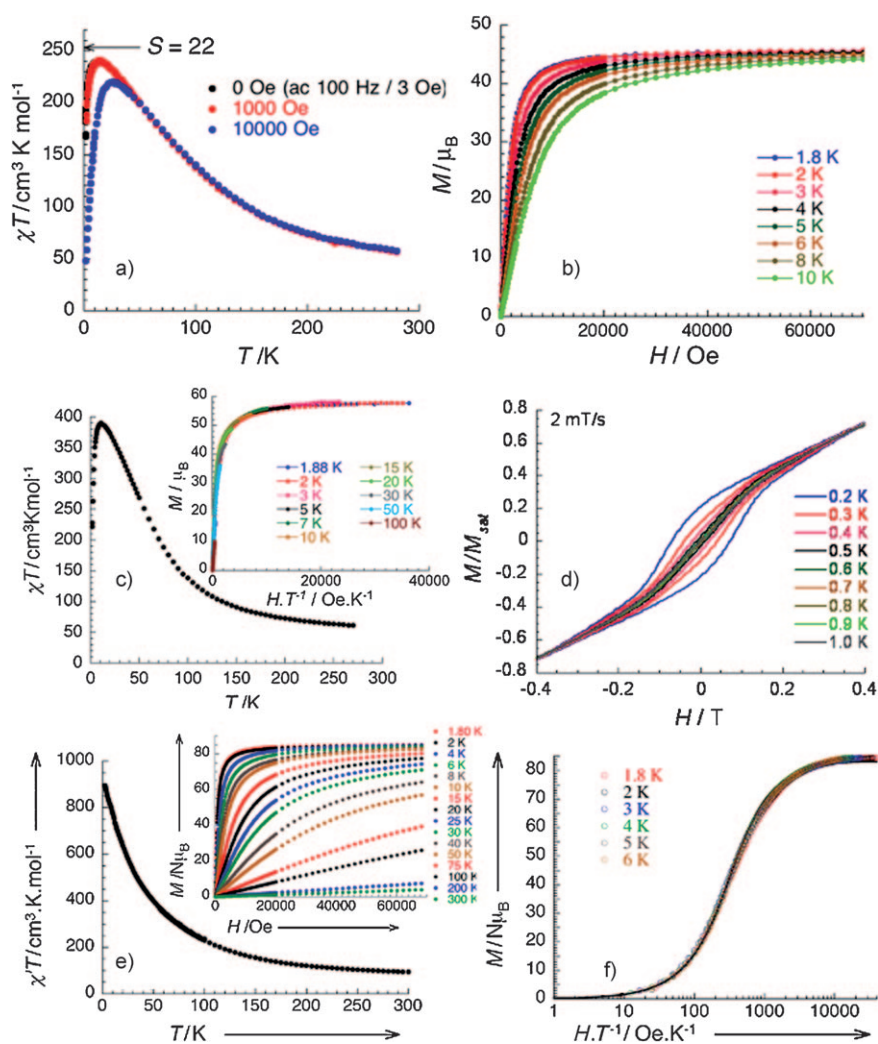


Figure 4. a) χT versus T plot for compound **1**; b) M versus H plot for compound **1**, at different temperatures; c) χT versus T , and M versus H/T plot (at inset) for compound **2**; d) magnetic hysteresis plot for compound **2** at ultralow temperatures; e) χT versus T , and M versus H plots at different temperatures (at inset) for compound **3**; f) M versus H/T plots for compound **3** and the solid line represents the best fit obtained with an $S = 83/2$ Brillouin function, are shown.

ground-spin state around $S_T = 28$ ($406 \text{ cm}^3 \text{ K mol}^{-1}$ with $g_{\text{av}} = 2$). However, this value cannot be so easily justified, as it is only an estimate and it assumes $g = 2$. Alternatively, a ground-spin state of $S_T = 27$ may also be possible ($378 \text{ cm}^3 \text{ K mol}^{-1}$ with $g_{\text{av}} = 2$) and may result from a situation in which the spins of two Mn^{II} are antiparallel to the spins of the rest of the Mn^{III} ions and the remaining four Mn^{II} ions. Thus, it was not possible to determine the ground-spin state of **2** precisely, but our measurements clearly indicate a spin of $S_T = 28 \pm 1$, which is quantitatively in agreement with both the low-temperature χT product and the magnetisation saturation value obtained from the M versus H data. This uncertainty in the determination of the spin state suggests that low-lying excited-spin states take part in the ordering process. Attempts to fit the M versus H/T data with Brillouin functions even after introducing S_T and D as adjustable parameters failed, probably as a result of inter-

molecular magnetic interactions. Below 1 K, magnetic hysteresis, that is, slow relaxation of the magnetisation, was observed and the coercivity was found to be approximately 1500 Oe at 0.2 K (Figure 4d). The hysteresis could arise from magnetic anisotropy and/or intermolecular interactions. We observed a much smaller hysteresis effect in compound **2** (below 0.5 K with a coercive field reaching 300 Oe at 0.04 K), which was found to have a positive D value,^[17] this effect must originate from intermolecular interactions. The hysteresis loops at higher temperatures for **2** (0.8–1 K) are indicative of some intermolecular interactions, showing a double-S-like curve typical for antiferromagnetic coupling. Therefore, the enhanced hysteresis could arise from the combination of both intermolecular effects and molecular anisotropy, resulting from the presence of an uncompensated JT axis in this edge-sharing arrangement of the two supertetrahedra. The fit to an Arrhenius plot leads to an effective energy barrier U_{eff} of 13.1 K and relaxation time of 2.0×10^{-10} s (see Figure S2 in the Supporting Information). A similar compound with different ligand has been reported recently by Tasiopoulos et al.^[23]



MeCN (**3**): The room-temperature value of the magnetic susceptibility and temperature product χT for **3** (Figure 4e) is $93 \text{ cm}^3 \text{ K mol}^{-1}$, which is much higher than the expected value ($66.625 \text{ cm}^3 \text{ K mol}^{-1}$ for $g_{\text{av}} = 2$) for twelve Mn^{III} ($S = 2$) and seven Mn^{II} ($S = 5/2$) ions. The high χT value suggests dominating ferromagnetic interaction between the manganese ions. Magnetisation studies show that the magnetisation saturates very fast above 1.5 T to reach about $84.5 \mu_{\text{B}}$ (inset of Figure 4e), close to the expected value of $83 \mu_{\text{B}}$ (with $g_{\text{av}} = 2$) for an $S_T = 83/2$ ground-spin state. At the high applied field, the magnetisation is fully saturated and no slope is observed, suggesting the absence of significant anisotropy in the compound. Moreover, the data in the 1.8–6 K temperature range presented as an M versus H/T plot (Figure 4f) are all superposed on one single master curve, sug-

gesting again the lack of significant magnetic anisotropy and indicates that the ground state is essentially the only one populated below this temperature. Despite possessing the highest ground-spin state found to date, this compound lacks any significant anisotropy,^[11] probably as a result of the relative orientation of the JT axes of the individual Mn^{III} ions.

The magnetothermal properties of the three complexes were studied by means of heat capacity $C(T,H)$ experiments. Figure 5 shows the obtained temperature-dependent behav-

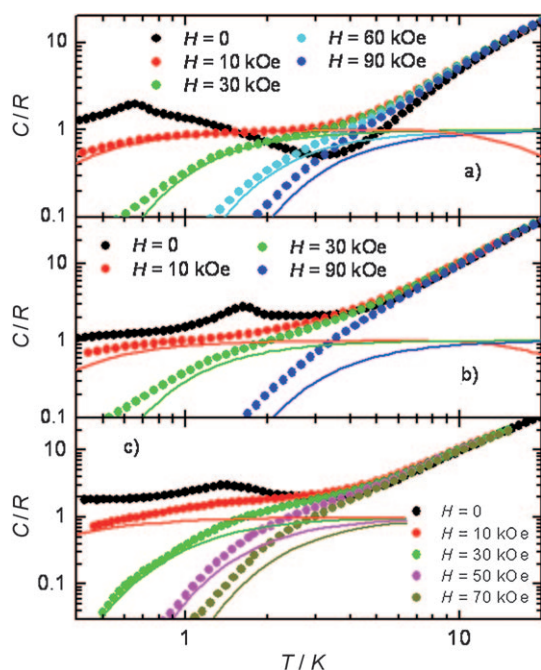


Figure 5. Temperature-dependencies of the heat capacity C normalised to the gas constant R at several applied fields, as labelled, for **1**, **2** and **3** (top, middle and bottom, respectively). Solid lines are the fits to the Schottky contributions (see text).

ours collected for several applied magnetic fields. At high temperatures, the heat capacities are dominated by non-magnetic contributions arising from thermal vibrations of the lattices. The main feature in the magnetic contributions is the observation of a peak in the zero-field data of each complex, indicating a phase transition to a long-range magnetic order. Its magnetic origin is indeed proved by the fact that this feature is quickly and fully suppressed in external fields. Specifically, the ordering temperatures occur at $T_c = 0.65$, 1.65 and 1.45 K for **1**, **2** and **3**, respectively. The occurrence of long-range magnetic order implies a negligible molecular magnetic anisotropy; otherwise superparamagnetic blocking would have occurred at a more elevated temperature, thereby inhibiting the phase transition.^[24] In terms of MCE, it is well established that negligible anisotropy is particularly favourable for obtaining large magnetic entropy changes. As a comparison with the experimental data, Figure 5a shows the calculated Schottky curves (solid lines)

arising from the field-splitting of the $S_T = 22$, 28 and $83/2$ multiplets for **1**, **2** and **3**, respectively. We assume $g = 2$ and negligible anisotropy for the three complexes. One can see that the calculated curves excellently reproduce the experimental behaviour reported for **1** and **3**, respectively, whilst the agreement is less satisfactory in case of **2**. This is likely because excited spin states other than $S = 28$ are accessible, as already discussed in the previous section.

We next evaluate the MCE for the three complexes. From the experimental heat capacity, the entropy $S(T,H)$ is obtained by integration over the temperature, that is, using Equation (3).

$$S(T, H) = \int_0^T \left\{ \frac{C(T, H)}{T} \right\} dT \quad (3)$$

The magnetic entropy change $\Delta S_m(T, H)$ can straightforwardly be estimated from Equation (3) for changes in the applied field. Note that the field-independent lattice contributions cancel out, since we deal with differences between entropies. Figure 6 shows that **1** has the maximum $-\Delta S_m$ of $10.3 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 2.6$ K for the applied-field change

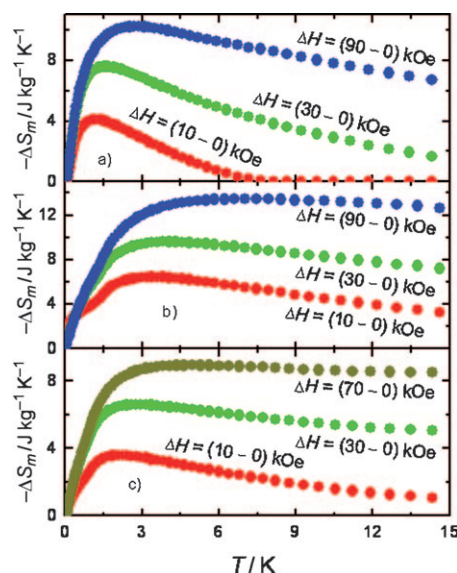


Figure 6. Temperature-dependencies of the magnetic entropy change ΔS_m for **1**, **2** and **3** (top, middle and bottom, respectively), as obtained from the heat capacity data of Figure 4.

$\Delta H = (90-0) \text{ kOe}$, **2** has the maximum $-\Delta S_m$ of $13.3 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 5.2$ K for $\Delta H = (90-0) \text{ kOe}$, and **3** has the maximum $-\Delta S_m$ of $8.9 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 4.2$ K for $\Delta H = (70-0) \text{ kOe}$. The fact that **2** has the larger MCE among the studied complexes should not come as a surprise. Indeed, it is more likely for this compound to have low-lying excited spin states, which provide a source of additional magnetic entropy. In terms of the MCE, this is an even more important factor than the high-spin value and the negligible anisotropy.^[12]

Conclusion

In conclusion, a series of structurally related polynuclear mixed-valence Mn complexes with very high ground-spin states were chosen for magnetic and magneto thermal studies. In fact, compound **3** possesses the highest ground-spin state so far discovered. The high spin and low magnetic anisotropy of the complexes were found as the main attractions for studying their magnetothermal behaviour, which shows that the compounds have long-range magnetic ordering temperatures at 0.65, 1.65, and 1.45 K, for **1**, **2**, and **3**, respectively. Among the three studied compounds, compound **2** is of special interest because it has the largest magnetocaloric effect. This is not unexpected and results from the presence of very small anisotropy, which is most probably due to the presence of one uncompensated JT axis in the edge-sharing supertetrahedra. Moreover, low-lying excited states provide a source of additional entropy, which likely is responsible for the higher MCE of compound **2**. In summary, the magnetothermal investigation of three structurally related high-spin, high-nuclearity, mixed-valence manganese compounds made up from Mn₁₀ supertetrahedra, has shown that large magnetocaloric effects and long-range orderings are possible.

Experimental Section

Synthesis: All chemicals were purchased from Aldrich and were used without any further purification.

Synthesis of compound 1: A few drops of triethylamine (16 drops) were added to a solution of pentane-1,3,5-triol (481 mg, 4 mmol) in MeCN (20 mL) and stirred for 5 min. MnBr₂·4H₂O (572 mg, 2 mmol) was added to the resulting solution, followed by the addition of anhydrous sodium acetate (80 mg, 1 mmol). The resulting solution was stirred for five minutes and then NaN₃ (130 mg, 2 mmol) was added. The slurry was then stirred for 30 min in room temperature, and then refluxed for 2 h and then cooled down to the room temperature and filtered. Slow evaporation of the filtrate resulted into black crystals in one week in a 45% yield.

Synthesis of compound 2: Compound **2** was synthesised according to the reported procedure.^[17] Pyridine (480 mL, 8 mmol) was added slowly to a slurry of MnCl₂·4H₂O (594 mg, 3 mmol), 2,2-dimethyl-1,2-propandiol (420 mg, 4 mmol) and sodium acetate (480 mg, 6 mmol) in acetonitrile (20 mL). After vigorous stirring for 2 h, the resulting light brown solution was allowed to evaporate slowly. Reddish-brown, rod-shaped crystals of compound **2** appeared in two weeks with a 26% yield.

Synthesis of compound 3: Compound **3** was also prepared according to the reported procedure.^[18] A solution of NaN₃ (200 mg, 3 mmol) in MeOH (5 mL) was added with stirring to a slurry of 2,6-bis(hydroxy-methyl)-4-methylphenol (1200 mg, 6 mmol), MnCl₂·4H₂O (0.4 g, 2 mmol), and sodium acetate (hydrated, 140 mg, 1 mmol) in MeCN (20 mL). After the mixture had been stirred for 1 h at room temperature, the mixture was heated at reflux for 2 h. The resulting dark brown solution was allowed to cool down and was filtered. After the solution had been left to stand in a sealed vessel for one week, well-formed black crystals of **3** were obtained with a 42% yield.

Magnetic measurements: Both dc and ac magnetic susceptibilities were measured on a Quantum Design MPMS-XL SQUID magnetometer. Diamagnetic corrections were applied for the sample holder, determined experimentally, and for the complexes, evaluated through Pascal's constants of all the constituent atoms, respectively. Magnetocaloric studies were

carried out with the PPMS in the range of 0 to 9 T, and 0.3 to 15 K on polycrystalline samples.

Acknowledgements

We would like to thank Dr. G. Wu and Dr. A. M. Ako for their contribution in producing compounds **1** and **3**, respectively, and the DFG (CFN) for funding. S.N. gratefully acknowledges the mobility grant from MAGMANet (grant No. 515767-2) to carry out the research in Karlsruhe, Leiden and Zaragoza. M.E. thanks the Spanish Ministry for Science and Innovation for grants MAT2009-13977-C03 and CSD2007-00010.

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Received: July 14, 2010
Published online: September 28, 2010