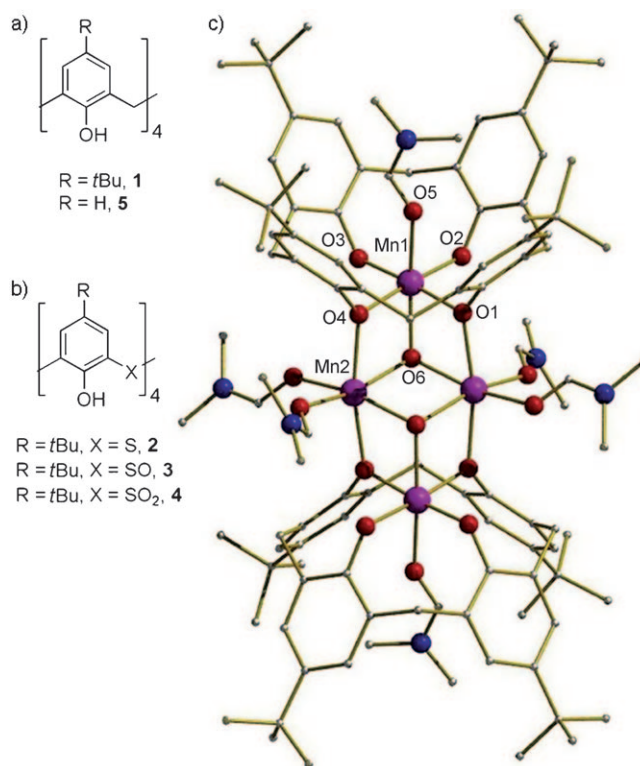


## A Calix[4]arene 3d/4f Magnetic Cooler\*\*

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The success with which coordination chemists have produced (often aesthetically pleasing) molecules with fascinating physical properties is derived from the systematic exploration of the effects of ligand design, metal identity, and heating regime upon cluster symmetry, topology, and nuclearity.<sup>[1]</sup> The design of molecular nanomagnets<sup>[2]</sup>—model systems with which to investigate the possible implementation of spin-based solid-state qubits<sup>[3]</sup> and molecular spintronics<sup>[4]</sup>—has been the subject of much interest in recent years because their molecular nature and inherent physical properties allow the crossover between classical and quantum physics to be observed.<sup>[5]</sup> The synthesis of new types of molecular nanomagnets therefore remains an exciting challenge, but the range of organic ligands employed thus far is surprisingly restricted.<sup>[6]</sup> Undoubtedly the most successful route has been to employ small, flexible polydentate ligands in self-assembly.<sup>[7]</sup> An alternative approach would be to entirely encapsulate the magnetic skeleton within a large rigid organic or inorganic sheath whose dual role could also include the introduction of redox activity, surface compatibility, or simply the removal/control of dipolar interactions.<sup>[8]</sup>

Calix[4]arenes (C4s) are typically bowl-shaped molecules which have been exploited in the formation of various nanometer-scale supramolecular architectures.<sup>[9]</sup> Their rigid conformations can be utilized in self-assembly, or combined with functionalization at the upper rim to present binding sites for assembly-directing metal centers.<sup>[9,10]</sup> The polyphenolic nature of these molecules therefore renders them good ligand candidates for the isolation of paramagnetic cluster compounds. In this regard only one cluster compound, having greater than four transition metals, has been shown to form



**Figure 1.** a) *para-tert*-Butylcalix[4]arene used in transition-metal cluster formation. b) Thiocalix[4]arenes used in transition- and lanthanide-metal cluster formation. c)  $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$  SMM formed with **1**.<sup>[14]</sup> Hydrogen atoms omitted for clarity.

with methylene-bridged *para-tert*-butylcalix[4]arene **1** (Figure 1 a).<sup>[11]</sup> Thiocalix[4]arenes and their oxidized derivatives **2–4** (Figure 1 b) possess additional donor atoms, and these have been used in the formation of a number of polynuclear transition-metal or Ln clusters.<sup>[12,13]</sup> The additional donor atoms (relative to **1**) around the molecular skeleton play a key role in supporting complex formation by taking part in the bonding within the metal-cluster framework.

For our purposes, readily accessible methylene-bridged C4s present the potential to 1) form novel cluster compounds at the lower rim of the bowl-shaped macrocycles, and 2) easily alter the upper-rim properties to access a vast library of new metal clusters containing supramolecular building blocks. These features may therefore allow control of the interactions between clusters (thereby modulating their orientation in the solid state), or variation of the degree of cluster isolation (or encapsulation) through alteration of the upper rim of the calix[4]arene. We have recently reported the formation of the first Mn cluster and the first single-molecule magnet (SMM) to be isolated using any methylene-bridged C4 (Figure 1 c).<sup>[14]</sup> The mixed-valent  $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$  complex is housed between two

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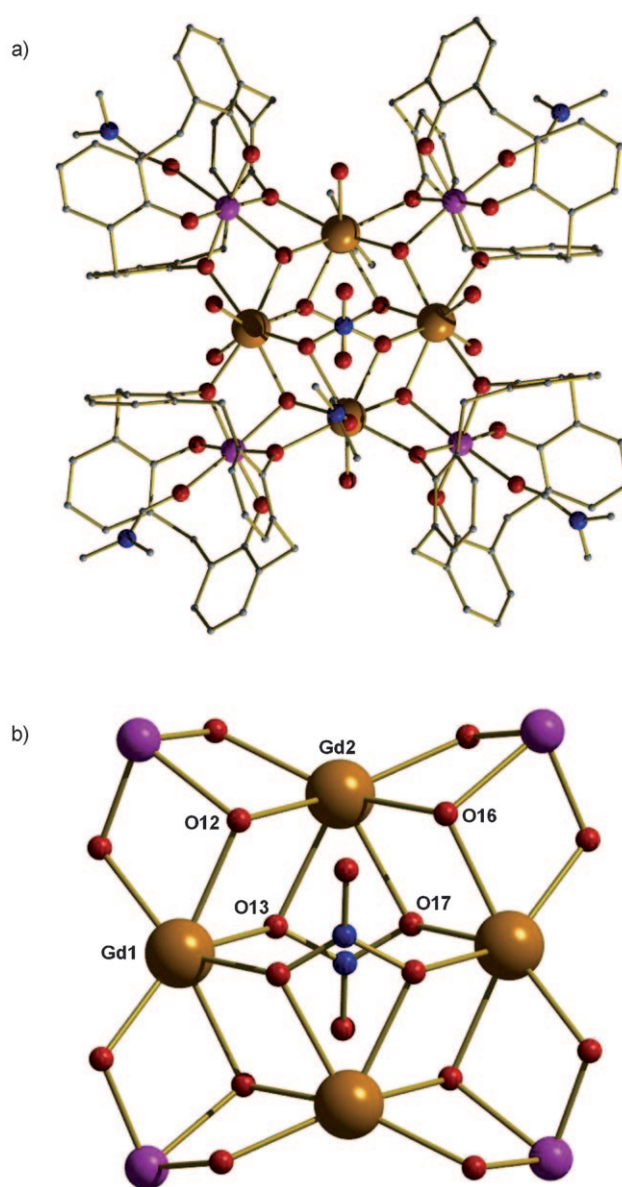
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molecules of either **1** or tetrahydrocalix[4]arene **5**, with the Mn<sup>III</sup> centers located within the planes of oxygen atoms found at the lower rims of C4 (Mn1). The Mn<sup>II</sup> centers and  $\mu_3$ -OH<sup>-</sup> ions form the remainder of the SMM, with additional *N,N*-dimethylformamide (dmf) ligands occupying Mn<sup>II</sup> coordination sites around the periphery of the assembly. These new types of SMM building blocks self-assemble into bilayer arrays with markedly different interlayer spacings, which are dictated by the upper-rim composition of the chosen C4 starting material.

Despite the examples highlighted above, there have (to our knowledge) been no literature reports of calix[4]arene-based mixed 3d/4f metal clusters.<sup>[15]</sup> Herein we show the facile formation of the first such cluster and describe its magnetic properties which demonstrate it to be a candidate for magnetic refrigeration at low temperatures.

The reaction of Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with **5** and NEt<sub>3</sub> in a solvent mixture of MeOH/DMF (1:1) results in the formation of the complex [Mn<sup>III</sup><sub>4</sub>Gd<sup>III</sup><sub>4</sub>(OH)<sub>4</sub>(**5**)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>(dmf)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>](OH)<sub>2</sub> (**6**), which crystallizes as purple blocks which are in the monoclinic space group *C2/c*. The cluster (Figure 2) comprises a near-planar octametallc core having a square of Gd<sup>III</sup> ions inside a square of Mn<sup>III</sup> ions. The four Gd ions are connected to each other through four  $\mu_3$ -OH<sup>-</sup> ions (O12 and O16 and their symmetry equivalents) and two  $\mu_3$ -NO<sub>3</sub><sup>-</sup> ions to create a central {Gd<sup>III</sup><sub>4</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>} unit. The  $\mu_3$ -OH<sup>-</sup> ions additionally bridge to the four {Mn<sup>III</sup>(**5**)(dmf)} corner units of the Mn<sub>4</sub> square. The  $\mu_3$ -**5** ligands are fully deprotonated with two oxygen atoms bonding terminally to the Mn<sup>III</sup> ions and two  $\mu$ -bridging to the central Gd<sub>4</sub> square. The Mn ions lie in distorted octahedral geometries in O<sub>6</sub> coordination spheres with the Jahn–Teller axes described by the dmf–Mn–OH vector; that is, across the diagonal of the Mn<sub>4</sub> square. The Gd<sup>III</sup> ions are eight coordinate and are in distorted square-antiprismatic geometries with the remaining sites filled by a combination of terminal H<sub>2</sub>O molecules, which form intramolecular H bonds to the terminally bonded O atoms of **5** and intermolecular H bonds to hydroxide ions, and dmf molecules.

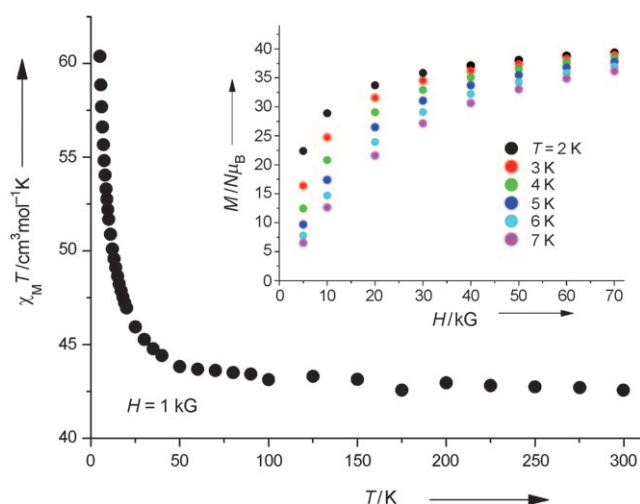
A notable feature of **6** is that the general Mn<sup>III</sup>C4 motif found in the Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub> SMM shown in Figure 1 c is preserved in this new mixed-metal complex. This motif shows that this is a favorable structural unit (“cluster ligand”), which may be exploited in the formation of other complexes and supramolecular architectures. Examination of the extended structure shows that symmetry equivalents of **6** pack in a complex fashion. As a result of the disorder of the solvent molecules within the crystal lattice, it is not possible to fully identify all of the intermolecular interactions occurring between the structural components. Although this is the case, there appear to be H-bonding interactions that bridge neighboring assemblies through the hydroxide ions. In addition, an interesting feature of the extended structure is that four Mn<sup>III</sup>**5** moieties from neighboring fragments pack so as to form dmf-rich microenvironments (see Figure S1 in the Supporting Information). These are somewhat reminiscent of hexameric calix[4]arene-based molecular capsules, suggesting that appropriately functionalized C4 clusters could be used to



**Figure 2.** a) Molecular structure of **6** showing the arrangement of molecules of **5** at the corners of the Mn<sub>4</sub> square. b) The magnetic core in **6** showing  $\mu_3$ -NO<sub>3</sub><sup>-</sup> ions and the square of Gd<sup>III</sup> ions within the square of Mn<sup>III</sup> ions. Purple Mn, brown Gd, red O, blue N, silver C. Hydrogen atoms are omitted for clarity.

form self-assembled structures containing large internal volumes.<sup>[9]</sup>

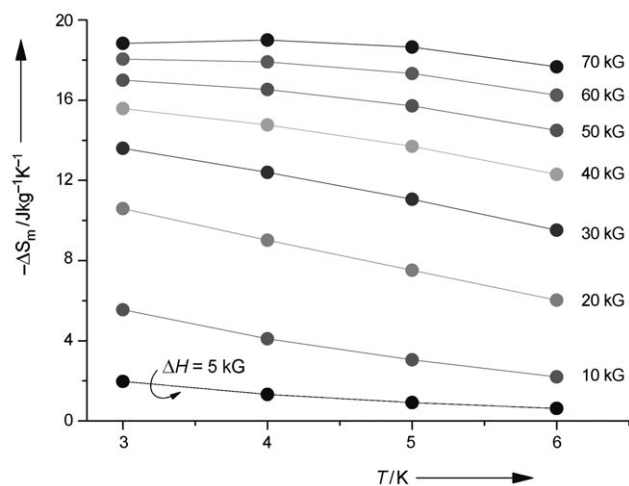
Direct current (dc) susceptibility measurements were carried out within the 5–300 K temperature range in an applied field of 1000 G. The room temperature  $\chi_M T$  value of approximately 42.8 cm<sup>3</sup> K mol<sup>-1</sup> is close to the spin-only ( $g = 2.0$ ) value of approximately 43.5 cm<sup>3</sup> K mol<sup>-1</sup>, expected for an uncoupled Mn<sup>III</sup><sub>4</sub>Gd<sup>III</sup><sub>4</sub> unit (Figure 3). The value stays essentially constant as the temperature is decreased, and at approximately 50 K the  $\chi_M T$  value increases, reaching a maximum of approximately 60.5 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K. This behavior is suggestive of very weak intramolecular exchange and one would expect nesting, and thus population of several *S* states even at the lowest temperatures studied. This is



**Figure 3.** Temperature dependence (5–300 K) of the dc molar susceptibility for **6** collected in an applied field of 1 kG. Inset: Magnetization of **6** versus field in the ranges  $T=2\text{--}7$  K and  $H=5\text{--}70$  kG.

reflected in the low-temperature  $\chi_M T$  value, which is below that expected for a ferromagnetically coupled cluster with an isolated  $S=22$  ground state ( $253\text{ cm}^3\text{ K mol}^{-1}$ ), and can also be seen in the magnetization versus field data (collected in the ranges 5–70 kG and 2–7 K and plotted in the inset of Figure 3) which shows  $M$  increasing only slowly with  $H$ , rather than quickly reaching saturation as one would expect for an isolated spin ground state. This data is indicative of the population of low-lying levels having a smaller magnetic moment, which only become depopulated with the application of a large field. Indeed even in a field of 70 kG,  $M$  does not reach saturation. A plot of reduced magnetization ( $M/N\mu_B$ ) versus  $H/T$  reveals the isofield lines to be almost superimposable (see Figure S2 in the Supporting Information), which is indicative of an isotropic cluster as one would expect from the molecular topology and the perpendicular alignment of the Jahn–Teller axes of the  $\text{Mn}^{\text{III}}$  ions. The above results suggest **6** to be an excellent candidate for magnetic refrigeration.<sup>[16]</sup>

Recent studies<sup>[17]</sup> of isotropic high-spin molecules have revealed a large magneto-caloric effect (MCE), that is, the change of the magnetic entropy  $\Delta S_m$  and adiabatic temperature following a change of the applied magnetic field. The interest in the MCE is both for fundamental reasons and for potential technological applications, since the MCE and the associated principle of adiabatic demagnetization can be efficiently exploited for cooling applications.<sup>[18]</sup> Although the MCE is intrinsic to any magnetic material, in only a few cases are the changes sufficiently large to make them suitable for applications. The key is finding the best performing refrigerant. In this respect, the feasibility of **6** requires the determination of  $\Delta S_m$  as a function of  $T$  as well as  $\Delta H$ . In an isothermal process of magnetization,  $\Delta S_m$  can be derived from Maxwell relations by integrating over the magnetic field change  $\Delta H = H_f - H_i$ , that is,  $\Delta S_m(T)_{\Delta H} = \int [\partial M(T, H) / \partial T]_H dH$ .<sup>[18b]</sup> From the experimental magnetization data of Figure 3, the obtained  $\Delta S_m$  is depicted in Figure 4 for several



**Figure 4.** Magnetic entropy change ( $\Delta S_m$ ) versus  $T$  for **6** for applied field changes  $\Delta H$ , as labeled.

field changes. It can be seen that  $-\Delta S_m$  increases gradually with increasing  $\Delta H$ , reaching a value of  $19.0\text{ J kg}^{-1}\text{ K}^{-1}$  at 4 K for the experimentally accessible maximum  $\Delta H$  of 70 kG. This value is amongst the highest values ever reported for this temperature range.<sup>[16–18]</sup> Notably, the observed magnetic entropy changes are much larger than the maximum allowable entropy for an isolated  $S=22$  spin ground state, that is,  $R \ln(2S+1) = 3.8R = 9.0\text{ J kg}^{-1}\text{ K}^{-1}$ , which demonstrates that the presence of low-lying excited spin states can have a strong and positive influence on the MCE. This example is the first of a molecular refrigerant containing gadolinium, an element which is widely employed in magnetic refrigeration.<sup>[18]</sup> Our results suggest that the synthesis of Gd clusters of higher nuclearity may provide a successful route to enhancing the already large MCE of this class of materials.

In conclusion we have demonstrated the facile formation of the first 3d/4f complex based on calixarene building blocks. The  $\text{Mn}^{\text{III}}/\text{calix}[4]\text{arene}$  structural motif present in the  $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$  SMM shown in Figure 1c is retained in the present structure and shows this to be a general unit for complex formation. Magnetic studies reveal that **6** has a large number of molecular spin states that are populated even at the lowest investigated temperatures, whereas the ferromagnetic limit  $S=22$  is being approached only at the highest applied fields. This result, combined with the high magnetic isotropy, enables the complex to be an excellent magnetic refrigerant for low-temperature applications. Exploration of other transition-metal, Ln, and mixed transition-metal/Ln clusters supported by methylene-bridged calix[4]arenes is underway to potentially tune the orientation of these new supramolecular building blocks in the solid state. Additional tuning of the assembly properties by exchange of lanthanide and transition metal may also be possible. These aspects of cluster design will be the focus of future studies.

### Experimental Section

$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.1 g, 0.39 mmol),  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 g, 0.22 mmol), and **5** (0.1 g, 0.23 mmol) were dissolved in a mixture of



DMF (10 cm<sup>3</sup>) and MeOH (10 cm<sup>3</sup>). The mixture was stirred for 5 min and then NEt<sub>3</sub> (0.2 g, 1.97 mmol) was added dropwise. The resulting purple solution was stirred for an additional hour. X-ray quality crystals were obtained in good yield (40%) after slow evaporation of the mother liquor. Elemental analysis (%) calculated for C<sub>130</sub>H<sub>140</sub>Mn<sub>4</sub>Gd<sub>4</sub>N<sub>8</sub>O<sub>40</sub>: C 47.27, H 4.27, N 3.39; found: C 47.02, H 4.14, N 3.27. Crystal data: C<sub>130</sub>H<sub>122</sub>Gd<sub>4</sub>Mn<sub>4</sub>N<sub>8</sub>O<sub>42</sub>, *M* = 3317.12, black block, 0.25 × 0.20 × 0.18 mm<sup>3</sup>, monoclinic, space group *C2/c* (No. 15), *a* = 34.41(3), *b* = 12.397(9), *c* = 32.15(4) Å, β = 98.14(3)°, *V* = 13576(22) Å<sup>3</sup>, *Z* = 4, Bruker Nonius X8 Apex II diffractometer, MoK<sub>α</sub> radiation, λ = 0.71073 Å, *T* = 100(2) K, 2θ<sub>max</sub> = 46.8°, 56018 reflections collected, 9621 unique (*R*<sub>int</sub> = 0.0831). Final *GoF* = 1.015, *RI* = 0.0462, *wR2* = 0.1217, *R* indices based on 7169 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>). The routine SQUEEZE was applied to the data due to the presence of badly disordered solvent molecules.<sup>[19]</sup> This had the effect of dramatically improving the agreement indices. CCDC 746739 (6) contains 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.

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