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Cryogenic Magnetocaloric Effect in a Ferromagnetic Molecular Dimer**

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Over the last few years, great interest has emerged in the synthesis and magnetothermal studies of molecular clusters based on paramagnetic ions, often referred to as molecular nanomagnets, in view of their potential application as low-temperature magnetic refrigerants.[1,2] What makes them promising is that their cryogenic magnetocaloric effect (MCE) can be considerably larger than that of any other magnetic refrigerant, for example, lanthanide alloys and magnetic nanoparticles.[3] The MCE is the change of magnetic entropy (ΔS_m) and related adiabatic temperature (ΔT_{ad}) in response to the change of applied magnetic field, and it can be exploited for cooling applications via a field-removal process called adiabatic demagnetization. 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 ideal molecular refrigerant comprises the following key characteristics:[1] 1) a large spin ground state S, since the magnetic entropy amounts to $R\ln(2S+1)$; 2) a negligible magnetic anisotropy, which permits easy polarization of the net molecular spins in magnetic fields of weak or moderate strength; 3) the presence of low-lying excited spin states, which enhances the field dependence of the MCE owing to the increased number of populated spin states; 4) dominant ferromagnetic exchange,[3c] favoring a large S and hence a large field dependence of the MCE; 5) a relatively low molecular mass (or a large metal/ligand mass ratio), since the nonmagnetic ligands contribute passively to the MCE. Although this last point is crucial for obtaining an enhanced effect, it has been mostly ignored to date. Molecular cluster compounds tend to have a very low magnetic density because of the large complex structural frameworks required to encase the multinuclear magnetic core.

Herein we propose a drastically different approach by focusing on the simple and well-known ferromagnetic molecular dimer gadolinium acetate tetrahydrate, $[\{Gd(OAc)_3(H_2O)_2\}_2]\cdot 4H_2O$ (**1**).[4a,b] The structure of **1** (Figure 1) comprises a dimer of Gd^{3+} ions bridged through two of the six carboxylate groups, which bond in an $\eta^2:\eta^1:\mu_2$-fashion.[4c] The remaining acetates are chelating, and the nine-coordinate (capped square-antiprismatic) geometry of the metal centers is completed by the presence of two terminally bound H_2O molecules. These partake in intramolecular hydrogen bonding to the neighboring chelating acetate ligands and are responsible for both the direct intermolecular H-bonds in the *ab* plane and the interplane H-bonds mediated by the lattice H_2O molecules (Figure S1 and Table S1 in the Supporting Information).

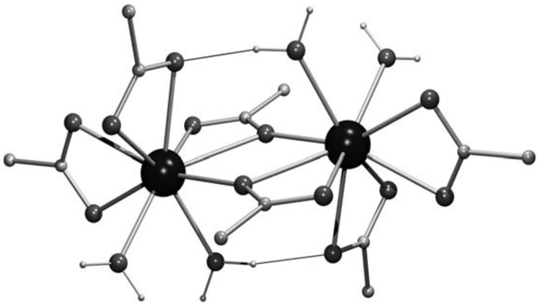

Figure 1. The molecular structure of **1**. Gd = black, O = dark gray, C = light gray, H = small bullets. H atoms of the methyl groups are omitted for clarity. Intramolecular hydrogen bonds are depicted as thin lines.

Our theoretical and experimental investigations (see the Supporting Information for details) of the magnetothermal properties of **1** down to millikelvin temperatures reveal a truly enormous MCE. In addition to magnetization and heat capacity experiments, which we employ to indirectly estimate the MCE, we make use of a homemade experimental setup that allows us to measure both ΔS_m and ΔT_{ad},[5] thus *directly* probing the extraordinary cooling performance of **1**.

Figure 2 depicts the direct-current (dc) magnetic susceptibility (χ) of **1** collected in an applied field $B_0 = 0.1$ T over the 2–140 K temperature range. The room-temperature experimental value of χT agrees with that expected from two non-

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Supporting information for this article, including experimental methods, the structure of **1** and views of the hydrogen-bonding networks, Monte Carlo numerical simulations of the magnetic ordering, and representative direct measurement of the temperature evolution of **1** under quasi-adiabatic conditions, is available on the WWW under http://dx.doi.org/10.1002/anie.201102640.

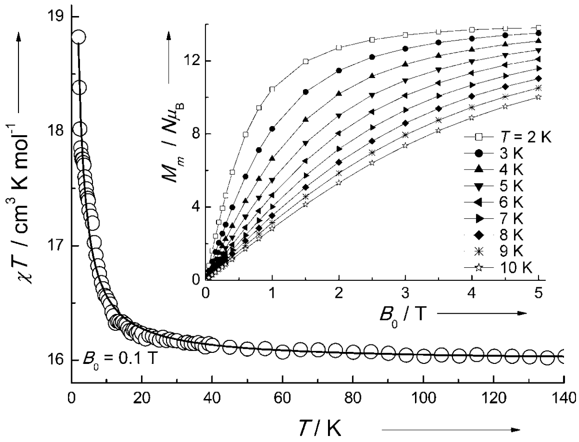

Figure 2. Temperature dependence ($T > 2$ K) of the dc susceptibility χT for **1** collected in an applied field of 0.1 T. Line is the fit, see text. Inset: magnetization of **1** versus applied field for several temperatures. Lines are guides to the eye.

interacting Gd^{3+} ions with $g = 2$, that is, $\chi T = 15.75\,cm^3\,K\,mol^{-1}$. On lowering T, χT stays nearly constant with decreasing temperature down to approximately 20 K, below which it increases significantly, reaching a value of $18.8\,cm^3\,K\,mol^{-1}$ at 2 K, thus corroborating the dominant ferromagnetic coupling between the two Gd^{3+} ions within each molecular unit. The isothermal molar magnetization (M_m, inset of Figure 2) shows a saturation value of $14.0\,N\mu_B$ (where N is the Avogadro constant and μ_B is the Bohr magneton) at the lowest investigated temperature of 2 K, in agreement with the ferromagnetic spin state $S = 7$. To estimate the intramolecular exchange constant, we fitted the experimental χT versus T curve (Figure 2) to a model based on the isotropic spin Hamiltonian $H = -J(S_{Gd1}S_{Gd2})$, obtaining $J/k_B = 0.068(2)$ K and $g = 2.01(1)$, in agreement with previous studies.[4b]

By Hall based micromagnetometry, we extended the magnetic measurements down to lower temperatures (Figure 3), with the isothermal $M_m(B_0)$ curve collected for $T = 0.2$ K (inset) supporting the dominant ferromagnetism of **1**. The temperature dependence of the dc susceptibility deviates from the Curie law at the lowest temperatures, giving rise to an anomaly centered at approximately 0.3 K for $B_0 = 0.01$ T. The slight decrease in χ below this temperature and the disappearance of the anomaly for fields higher than 0.1 T (Figure 3) suggest that the complex undergoes a transition to a magnetically ordered phase in which ferromagnetic interactions are important.

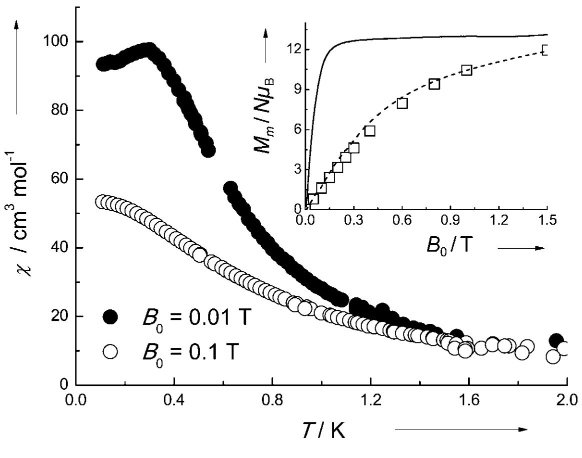

Figure 3. Low-temperature ($T \leq 0.2$ K) Hall micromagnetometry for **1**. Temperature dependence of the dc-susceptibility χ collected in applied fields of 0.01 and 0.1 T. Inset: experimental molar magnetization versus applied field for Hall micromagnetometry at 0.2 (——) and at 2.0 K (-----) and for SQUID magnetometry at 2.0 K (□).

To further elucidate the mechanism of magnetic ordering, we have performed numerical simulations according to the standard Metropolis Monte Carlo algorithm.[6] We considered each Gd_2 complex as an isotropic point dipole, that is, we assume a ferromagnetic $J = \infty$ intramolecular $Gd^{3+}\cdots Gd^{3+}$ exchange coupling and no intermolecular exchange paths. In satisfactory agreement with the experimental observations, we obtain a critical temperature of approximately 0.18 K for $B_0 = 0$ and a magnetic structure formed by alternating ferromagnetic *ab* planes (see the Supporting Information).

We next turn to the evaluation of the magnetothermal properties of **1** by presenting its experimental heat capacity (C). Figure 4 (top) depicts the experimental temperature dependence of C for selected applied fields. At high temperatures the heat capacity is dominated by nonmagnetic contributions arising from thermal vibrations of the lattice, which can be modeled with the six-fold Debye function (dashed line in Figure 4), yielding a value of $\Theta_D = 61.6$ K for the Debye temperature, typical for this class of cluster compound.[7] At low temperatures the applied field splits the molecular spin multiplet $S = 7$, gradually decoupling the intramolecular $Gd^{3+}\cdots Gd^{3+}$ exchange coupling and giving rise to a broad (Schottky-type) feature, which shifts to higher T by increasing B_0. Unfortunately, the experimentally accessible

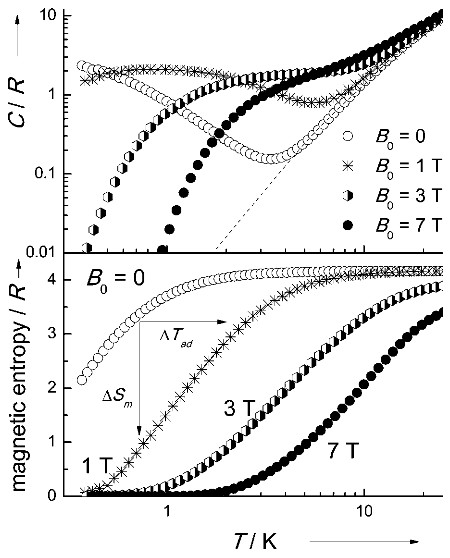

Figure 4. Top: temperature dependencies of the heat capacity of **1** normalized to the gas constant R collected for $B_0 = 0$, 1, 3, and 7 T. Bottom: temperature dependencies of the experimental magnetic entropy for several B_0, as obtained from the respective heat capacity data after subtracting the lattice contribution (dashed line).

temperatures do not permit the observation of the phase transition. We note, however, that the zero-field C keeps increasing by decreasing T in the lowest temperature region, reaching values exceeding that expected for magnetically isolated Gd_2 units ($\cong 1.9\,R$). From the experimental heat capacity, the temperature dependence of the magnetic entropy (S_m) is obtained by integration, using $S_m(T) = \int C_m/T\,dT$, where the magnetic heat capacity C_m is obtained from C upon subtracting the lattice contribution. The thus obtained $S_m(T)$ curves are shown in the bottom panel of Figure 4 for the corresponding applied fields. As expected, S_m for $B_0 > 0$ tends to the maximum entropy value per mole involved at high temperatures, corresponding to two Gd^{3+} $S = 7/2$ spins ($2\,R\ln(2s+1) \cong 4.16\,R$). In the case of $B_0 = 0$, our experimental blindness for T lower than approximately 0.35 K forced us to add a constant value to the zero-field $S_m(T)$ to match the limiting value at high T. As we shall see below, this crude procedure does not jeopardize our evaluation of the MCE of **1**.

From the S_m data, it is then straightforward to obtain the changes of magnetic entropy and adiabatic temperature, both indicated by arrows in Figure 4. The results are shown in Figure 5 as a function of T and for several field changes $\Delta B_0 = B_f - B_i$, where f and i indicate final and initial states, respectively. A striking result is the $-\Delta S_m$, which can be seen to reach values over 40 J kg^{-1} K^{-1} at $T \approx 1.8$ K for $\Delta B_0 = 7$ T, which is much larger than any other value reported in the recent literature.[3] We note that $-\Delta S_m$ approaches the maximum entropy value per mole ($4.16\,R \cong 42.5$ J kg^{-1} K^{-1}) for two fully decoupled Gd^{3+} ions. If ΔB_0 is lower than or of the order of the strength of the ferromagnetic intramolecular $Gd^{3+}\cdots Gd^{3+}$ exchange coupling, then the low-temperature value of $-\Delta S_m$ is much larger than can be produced in the absence of such a coupling. For instance, a relatively modest $\Delta B_0 = 1$ T is already sufficient to provide a $-\Delta S_m$ as large as 27 J kg^{-1} K^{-1} at $T \approx 0.5$ K. This remarkable field dependence of the MCE is also observed in ΔT_{ad}. Figure 5 (bottom) shows that $\Delta B_0 = 7$ T provides a maximum $\Delta T_{ad} = 12.7$ K for the same temperatures at which we observe the $-\Delta S_m$ maxima. By lowering ΔB_0 to 3 and 1 T, ΔT_{ad} decreases to 9.0 and 3.5 K, respectively. Therefore, the field dependence of ΔT_{ad} increases from nearly 2 to well over 3 K T^{-1}, respectively, setting this material as the most efficient refrigerant for this low-temperature region.[8]

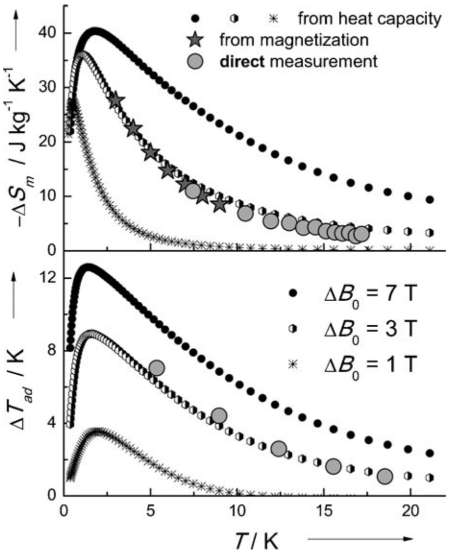

Figure 5. Top: temperature dependencies of the magnetic entropy change $\Delta S_m(T)$ as indirectly obtained from heat capacity and magnetization data, together with the direct measurements (gray dots) for the indicated applied-field changes ΔB_0. Bottom: temperature dependencies of the adiabatic temperature change $\Delta T_{ad}(T)$ as indirectly obtained from heat capacity data, together with the direct measurements, for the indicated ΔB_0.

In addition to heat capacity, magnetization data can also be employed for estimating ΔS_m by making use of the Maxwell relation, $\Delta S_m(T) = \int[\partial M_m(T,B_0)/\partial T]dB_0$. From the isothermal $M_m(B_0)$ curves of Figure 2, the so-obtained $\Delta S_m(T)$ value for $\Delta B_0 = 3$ T is displayed in Figure 5 (top) and can be seen to be in perfect agreement with the data obtained from C, thus demonstrating that our experimental uncertainty in the zero-field $S_m(T)$ does not affect the evaluation of ΔS_m and ΔT_{ad} of **1**. However, we note that both indirect procedures we followed for obtaining the MCE rely on numerical integrations that, by their nature, can be the source of large errors.[9] To overcome any possible shortfall inherent to these approaches, we have also measured ΔS_m and ΔT_{ad} directly under quasi-adiabatic conditions (see Figure S3 in the Supporting Information).[5] By again considering $\Delta B_0 = 3$ T, we obtain the ΔS_m and ΔT_{ad} values depicted in Figure 5, which rather beautifully corroborate our previous estimates.

In conclusion, an unprecedentedly large magnetocaloric effect at extremely low temperature is reported to occur in the simple ferromagnetic molecular dimer gadolinium acetate tetrahydrate. The magnetic ordering originates from dipolar coupling, and its collective magnetic behavior is somewhat reminiscent of that reported for gadolinium sulfate octahydrate, a well-studied, purely dipolar system, which was the subject of the very first adiabatic demagnetization experiments.[10] The enormous advantage of **1** over this prototype magnetic coolant is the intramolecular ferromagnetic exchange coupling, which favors the field-dependent enhancement of the magnetocaloric effect.

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