

Large Magnetocaloric Effect in a Wells–Dawson Type $\{\text{Ni}_6\text{Gd}_6\text{P}_6\}$ Cage**

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Magnetic refrigeration is based on the magnetocaloric effect (MCE) which relies on the entropy change of a material when placed in a magnetic field.^[1] High-spin isotropic magnetic molecules have recently been examined in this context.^[2–8] The very large MCE observed for some cages suggests they could replace the expensive and rare helium-3 in some applications.

Recently, paramagnetic metal ions are found in high-symmetry cages such as the keplerate,^[9] and this leads to exotic magnetic phenomena associated with the perfect spin-frustrated topology.^[10] Geometric frustration enhances the field dependence of the MCE due to the increased number of populated spin states.^[11] Phosphonate as a tridentate ligand can form pseudo-spherical cages due to the appropriate O–P–O angles (usually between 100° and 120° when coordinated).^[12] We have used these ligands to construct cobalt–gadolinium grid-like complexes,^[13] in which four-coordinate Co^{II} ions lead to formation of planar structures rather than cages. Here we report similar chemistry with Ni^{II} .

Reacting benzylphosphonic acid ($\text{H}_2\text{O}_3\text{PCH}_2\text{Ph}$) with two precursors, $[\text{Ni}^{\text{II}}_2(\mu\text{-OH})_2(\text{O}_2\text{CtBu})_4](\text{HO}_2\text{CtBu})_4$ ^[14] and $[\text{Ln}_2(\text{O}_2\text{CtBu})_6(\text{HO}_2\text{CtBu})_6]$ ($\text{Ln} = \text{Gd}, \text{Dy}, \text{and Y}$)^[15] we are able to obtain a family of molecular cages $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}_6(\text{OH})_2(\text{O}_3\text{PCH}_2\text{Ph})_6(\text{O}_2\text{CtBu})_{16}(\text{MeCO}_2\text{H})_2](\text{MeCN})_4$, where $\text{Ln} = \text{Gd}$ **1**, Dy **2**, and Y **3**. While the structures are heterometallic, in many ways the closest structural analogues in the literature are the homometallic Wells–Dawson polyoxometallates.^[16]

Compounds **1–3** crystallize in the space group $P2_1/n$ and are isomorphous. We describe the structure of **1** as representative. It features a centrosymmetric rugby-ball core (Figure 1).^[17] The two ends of the rugby-ball are capped by

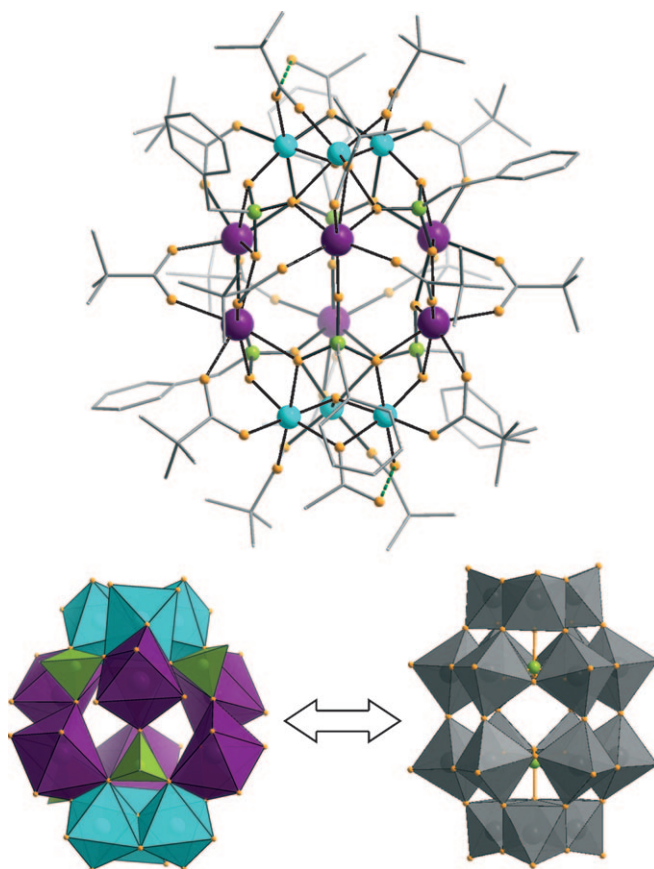


Figure 1. Upper: the structure of **1–3** in the crystal. Color codes: Ln, purple; Ni, cyan; P, green; O, orange; C, gray. Hydrogen bonds are illustrated with dotted green line. Lower: polyhedral representation of the core of $\text{Ni}_6\text{Gd}_6\text{P}_6$ (left) and a Wells–Dawson ion (right).

a $\{\text{Ni}_3(\mu_3\text{-OH})\}$ triangle, in which the $\mu_3\text{-OH}$ group is displaced by 0.48 Å out of the Ni_3 plane. There are two 2.11 pivalates^[18] and one 2.20 acetate ligand bridging the edges of these triangles (see Figure S1 in the Supporting Information). The presence of the μ -acetato O makes one edge of the Ni_3 triangle shorter ($\text{Ni}\cdots\text{Ni}$ 3.14 Å) than the other two ($\text{Ni}\cdots\text{Ni}$ 3.43 Å). Besides, the other acetato O of the acetate is protonated and forms a hydrogen bond with a adjacent pivalato O ($\text{O}\cdots\text{O}$ 2.84 Å). The presence of the acetate is probably from the hydrolysis of the acetonitrile during solvothermal synthetic condition, which has been previously observed.^[19]

The inner side of the Ni_3 triangles are bound to O atoms from three phosphonates and three pivalates. The phosphonates adopt either 5.222 or 5.221 coordination modes, binding

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[**] Y.Z.Z. is grateful for the support of Marie Curie International Incoming Fellowship (EC contract no: PIIF-GA-2008-219588). M.E. acknowledges the MICINN for contracts MAT2009-13977-C03 and CSD2007-00010. R.E.P.W. is grateful to the Royal Society for a Wolfson Merit Award. We thank Prof. Eric McInnes for helpful discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201008074>.

three adjacent Gd^{III} and two Ni^{II} ions, while the pivalates use either 2.11 or 2.21 coordination mode bridging one adjacent Gd^{III} and one Ni^{II} ion with a Ni...Gd separation of either 3.50 Å or 3.24 Å, respectively. The alternating arrangement of the Gd and the P atoms forms a Gd₃P₃ six-member ring, which connects to its centrosymmetric-related counterpart through six 2.11 pivalates. The Gd...Gd separations within the Gd₃P₃ six-member ring are around 6.2 Å, whereas between the Gd₃P₃ six-member ring are in the range of 3.9–4.9 Å. Interestingly, if the P atoms are included in the core of **1** it produces a {Ni₆Ln₆P₆} cage that resembles the Wells–Dawson polyoxometallate (lower half of Figure 1). This compliments the paramagnetic “Keggin” ions that have been reported.^[20]

The magnetic behavior of **1** to **3** has been studied on polycrystalline samples (Figure 2). At room temperature in each case, the $\chi_M T$ value is a little larger than the calculated value: for **1**, observed 55.3 emu K mol^{−1} (calcd 54.1 emu K mol^{−1} for six $S = 1$, $g = 2.2$ and six $S = 7/2$, $g = 1.99$ centers); for **2**, observed 93.6 emu K mol^{−1} (calcd 92.3 emu K mol^{−1} for six $S = 1$, $g = 2.2$ and six $S = 5/2$, $L = 5$, $g = 4/3$ centers); for **3**, observed 7.9 emu K mol^{−1} (calcd 7.3 emu K mol^{−1} for six $S = 1$, $g = 2.2$ centers). The difference may be due to ferromagnetic exchange. Upon cooling, for **1**, χT remains constant to 100 K before increasing to a maximum of 57.0 emu K mol^{−1} at 14 K. Below this temperature χT falls to 46.1 emu K mol^{−1} at 2 K. Magnetization measurements on **1** at low temperatures (2 to 10 K) were also performed (insert of Figure 2a). The magnetization (M) reaches 55.3 μ_B at 7 T at 2 K, which is the expected saturation value considering six $S = 1$, $g = 2.25$ and six $S = 7/2$, $g = 1.99$ centers. For **2**, χT vs. T curve decreases significantly with T to a minimum of 85.4 emu K mol^{−1} at 12 K before it increases to a value of 85.9 emu K mol^{−1} at 7 K. The decrease of χT at higher temperature region is associated with crystal field effects of the Dy^{III} ion.^[21] The M vs. H plots from 2 to 7 K (insert of Figure 2b) show a steady increase that reaches 45.3 μ_B at 7 T at 2 K without saturation.

Compound **3** allows us to study the magnetic interactions between the Ni centers. The χT product of **3** rises gradually to a maximum of 10.6 emu K mol^{−1} at 8 K before sharply decreasing to 8.0 emu K mol^{−1} at 2 K. The behavior of χT and the low-temperature M vs. H behavior was modeled using MAGPACK^[22] and the Hamiltonian below which assumes there are two equivalent non-interacting Ni₃ triangles (see the coupling scheme inserted in Figure 2c):

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3) - 2J_2(\hat{S}_2\hat{S}_3) + D \sum_{i=1}^3 \hat{S}_{iz}^2 + g\mu_B H \sum_{i=1}^3 \hat{S}_i \quad (1)$$

The best simulation (solid line in Figure 2c) gives $J_1 = 2.83$ cm^{−1}, $J_2 = -1.18$ cm^{−1}, $D = 5.7$ cm^{−1}, and $g = 2.28$. This model gives unequal magnetic interactions within the {Ni₃} triangle, and we assume the unique anti-ferromagnetic exchange occurs for the unique edge bridged by the 2.20 acetate. The large D value of the Ni^{II} ions, particularly compared to the J values, indicates that we do not have a well-isolated spin ground state (the calculation gives the first excited energy level lying ca. 3.0 cm^{−1} above the ground state).

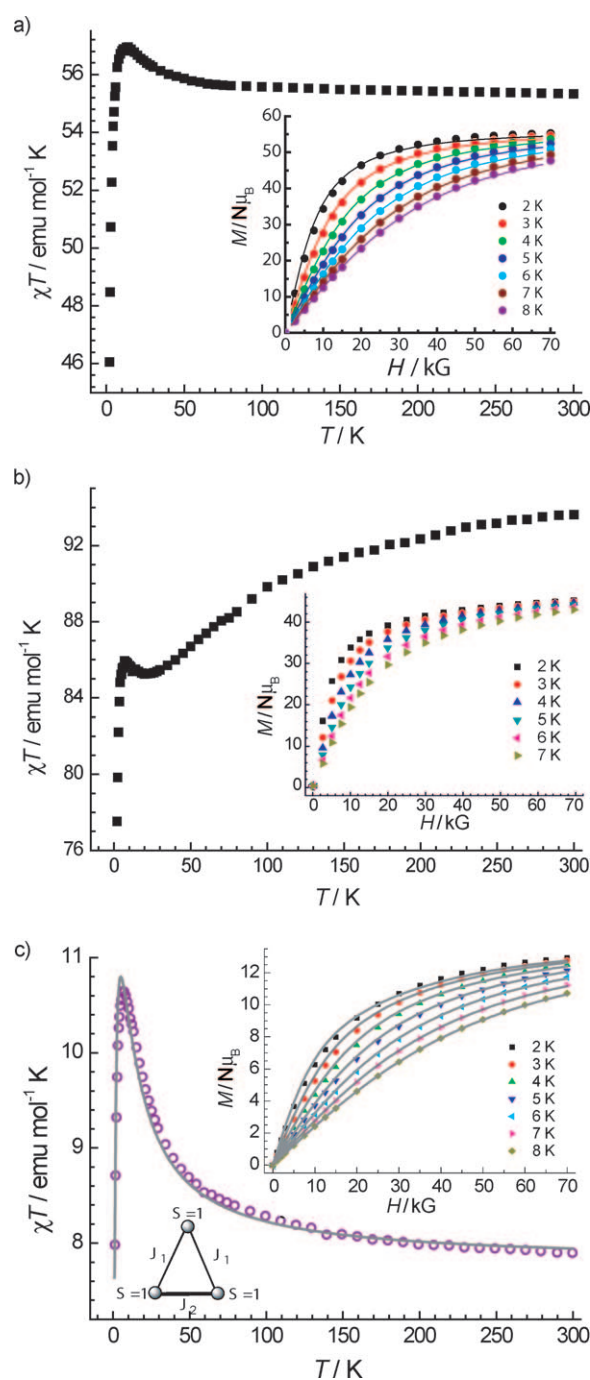


Figure 2. a) The χT vs. T plot of **1** under 5 kG dc field. Inset: the field-dependent experimental magnetization plots at indicated temperatures, together with the calculated simulation as obtained by adding six non-interacting paramagnetic Gd^{III} ions to the magnetization of **3**. b) The χT vs. T plot of **2** under 1 kG dc field. Inset: the field-dependent magnetization plots at indicated temperatures. c) The χT vs. T plot of **3** under 5 kG dc field. Inset: the field-dependent magnetization plots at indicated temperatures (upper) and the coupling scheme used for simulation (lower). Solid gray lines in (c): simulation curve by using the model described in the text.

The magnetic data suggest that the lanthanide ions are only very weakly coupled to the two {Ni₃} triangles. This is demonstrated by the fact that the magnetization of **1** can be

reproduced by adding a Brillouin curve for each of the six Gd^{III} ions to the magnetization of **3** (insert of Figure 2a). Very weak antiferromagnetic exchange of either Ni^{II}–Ln^{III} or Ln^{III}–Ln^{III} may be present, as suggested by the sudden drop of the experimental χT for **1** at the lowest temperatures.

Studies of the ac susceptibility for **1–3** show no slow-relaxation of magnetization down to 1.8 K, so these are not single molecule magnets. As the MCE can be described as $\Delta S(T)\Delta H = \int [\partial M(T, H) / \partial T]_H dH$ ^[11,6] **1** and **2** are candidates for

magnetic cooling. Calculating the entropy changes obtained from the magnetization data (Figure 3) gives values at 3 K and for a field change $\Delta H = 70$ kG of: for **1**, 26.5; for **2**, 12.2; for **3**, 5.6 J kg^{−1} K^{−1}. The entropy change of **1** is much larger than the value reported for previous 3d–4f compounds at 4 K^[5,13] and slightly higher than the highest value reported (25 J kg^{−1} K^{−1}) for a {Mn₁₄} cage.^[3b] It is noticeable that the smallest MCE is found for **3**, which indicates the much larger entropy changes in **1** and **2** are due to the lanthanide ions.^[3b,5]

The maximum entropy value per mole corresponds to $n = 6$ Ni^{II} spins $s = 1$ and, either, 6 Dy^{III} spins $s = 5/2$ or 6 Gd^{III} spins $s = 7/2$, and is calculated as $nR \ln(2s+1) = 19.1, 17.4$ and $6.6 R$, which correspond to 37.4, 33.8 and 14.3 J kg^{−1} K^{−1}, for **1**, **2** and **3**, respectively. For **1** the presence of isotropic Gd^{III} ions means we approach the maximum value (observed value 26.5 J kg^{−1} K^{−1}) but for **2** and **3** the anisotropy of the Ni^{II} and, especially Dy^{III} ions leads to a significantly lower observed value. Comparing the temperature dependency for **1** and **2**, the maximum in the magnetic entropy change shifts to higher temperature for **2**.^[8]

There has been a great deal of recent work on paramagnetic phosphonate cages;^[23] 3d–4f heterometallic cages reported using these ligands remain unusual.^[13,24,25] The Ni–Gd cage reported here shows huge low- T MCE, which should motivate further studies.

Experimental Section

See Supporting Information for detailed synthetic information. In outline: Compounds **1**, **2**, or **3** were obtained by mixing [Ni^{II}₂-(μ-OH₂)(O₂CrBu)₄](HO₂CrBu)₄ (0.1 mmol), [Ln₂(O₂CrBu)₆-(HO₂CrBu)₆] (0.075 mmol), and H₂O₃PCH₂Ph (0.1 mmol) in MeCN (8 mL) and stirring at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 °C for 12 h and then cooled to room temperature in a rate of 0.05 °C min^{−1}. Block-shape crystals formed from the reaction. Yields: **1**, 77%; **2**, 85%; **3**, 70%.

Received: December 21, 2010

Published online: March 25, 2011

Keywords: cage molecules · magnetocaloric effect · molecular refrigerants · phosphonates · polyoxometalates

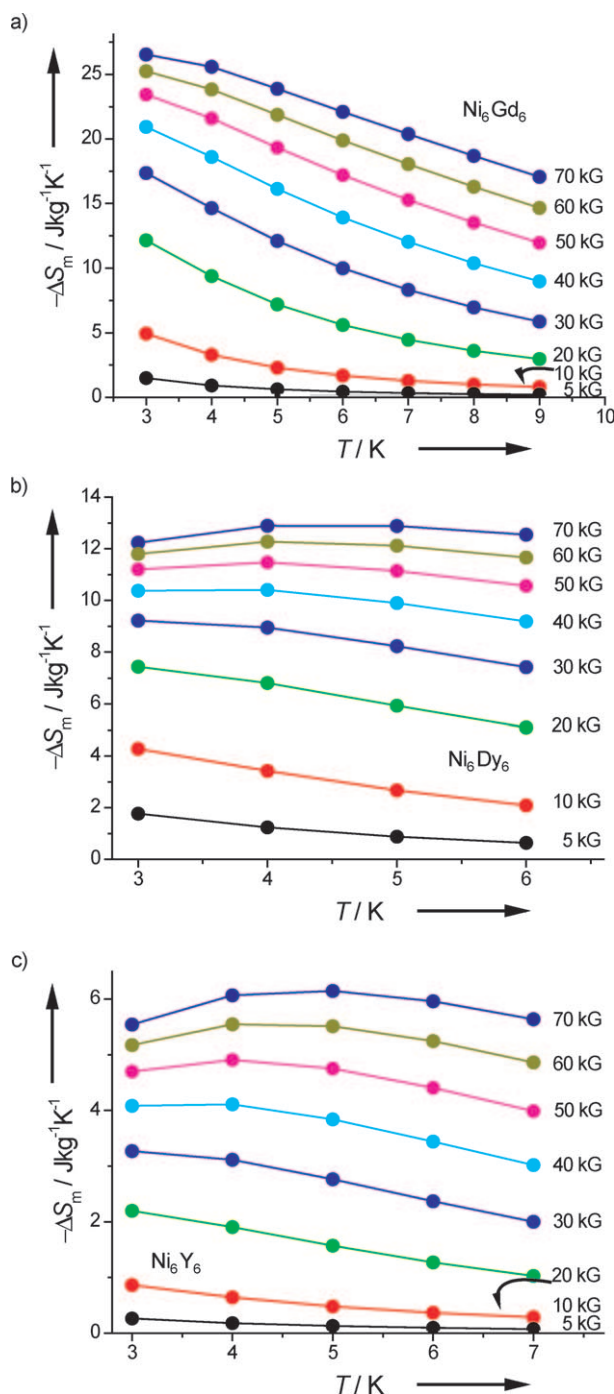


Figure 3. Calculation of ΔS_m for **1–3** at various fields and temperatures.

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