Molecular Coolers

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Large Magnetocaloric Effect in a Wells–Dawson Type $\{Ni_6Gd_6P_6\}$ 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 ($H_2O_3PCH_2Ph$) with two precursors, $[Ni^{II}_2(\mu\text{-}OH_2)(O_2C\textit{t}Bu)_4]\cdot(HO_2C\textit{t}Bu)_4$[14] and $[Ln_2(O_2C\textit{t}Bu)_6(HO_2C\textit{t}Bu)_6]$ (Ln = Gd, Dy, and Y),[15] we are able to obtain a family of molecular cages $[Ni^{II}_6Ln^{III}_6(OH)_2(O_3PCH_2Ph)_6(O_2C\textit{t}Bu)_{16}(MeCO_2H)_2](MeCN)_4$, where Ln = 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 a $\{Ni_3(\mu_3\text{-}OH)\}$ triangle, in which the μ_3-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 (Ni···Ni 3.14 Å) than the other two (Ni···Ni 3.43 Å). Besides, the other acetato O of the acetate is protonated and forms a hydrogen bond with a adjacent pivalato O (O···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

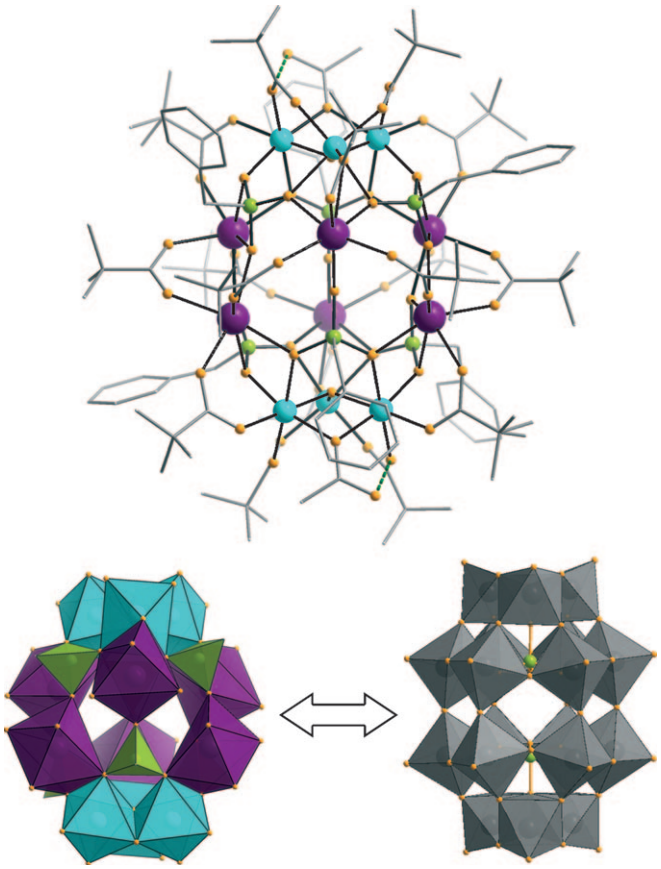

Figure 1. Upper: the structure of **1**–**3** in the crystal. Color codes: Ln, purple; Ni, cyan; P, green; O, orange; C, gray. Hydrogen bondings are illustrated with dotted green line. Lower: polyhedral representation of the core of $Ni_6Gd_6P_6$ (left) and a Wells–Dawson ion (right).

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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 Gd_3P_3 six-member ring, which connects to its centrosymmetric-related counterpart through six 2.11 pivalates. The Gd···Gd separations within the Gd_3P_3 six-member ring are around 6.2 Å, whereas between the Gd_3P_3 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 $\{Ni_6Ln_6P_6\}$ 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 Ni_3 triangles (see the coupling scheme inserted in Figure 2c):

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

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 $\{Ni_3\}$ 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).

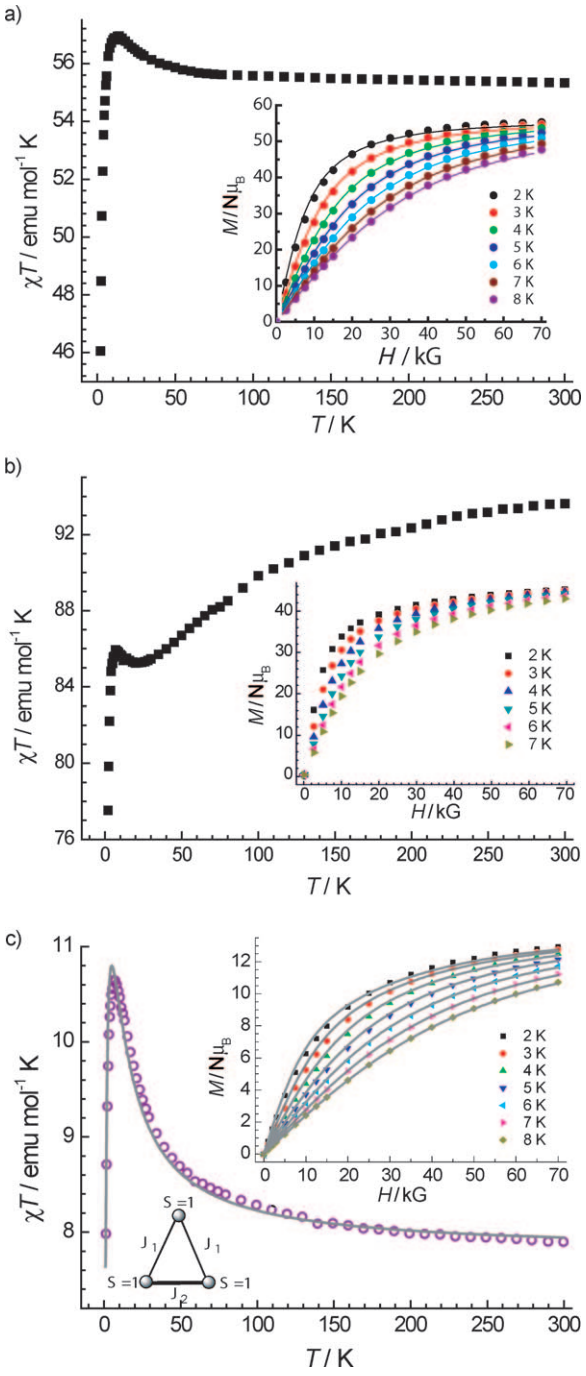

Figure 2. a) The χT vs. T plot of **1** under 5 kG dc field. Inset: the field-dependent experimental magnetization plots at indicated temperatures, together with the calculated simulation as obtained by adding six non-interacting paramagnetic Gd^{III} ions to the magnetization of **3**. b) The χT vs. 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 $\{Ni_3\}$ 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 $\Delta S(T)\Delta_H = \int[\partial M(T,H)/\partial T]_H dH$[1,6] **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 $\{Mn_{14}\}$ 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]

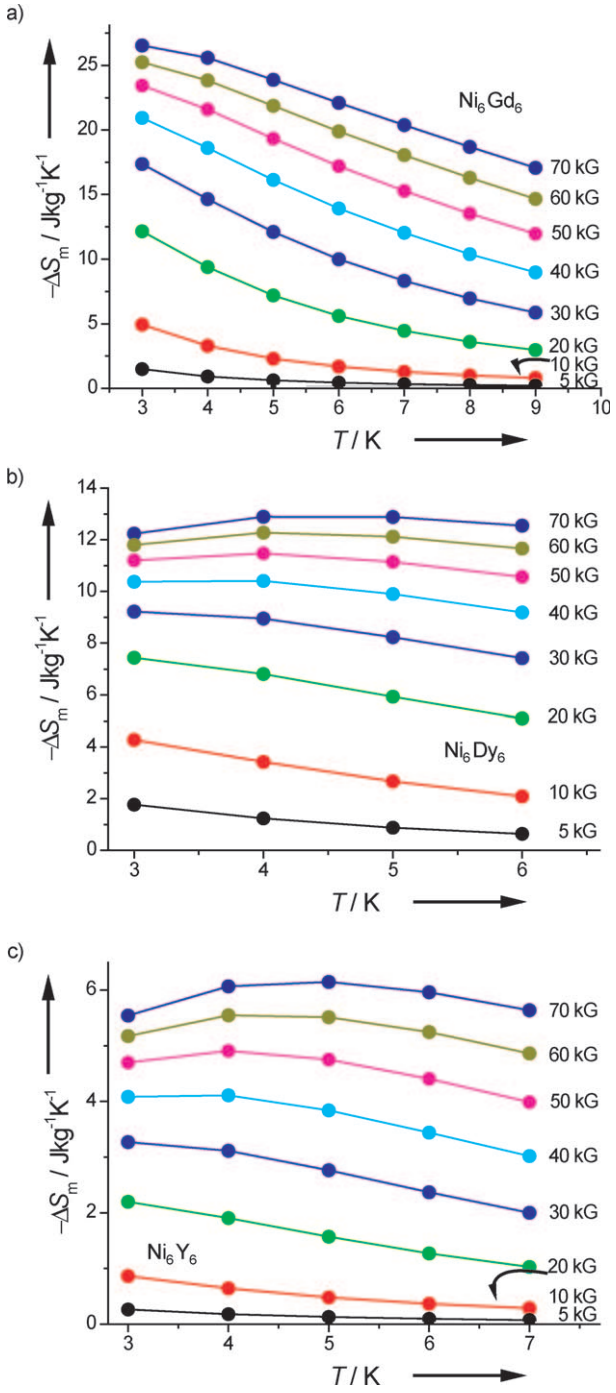

Figure 3. Calculation of ΔS_m for **1**–**3** at various fields and temperatures.

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 $[Ni^{II}_2(\mu\text{-}OH_2)(O_2CtBu)_4]\cdot(HO_2CtBu)_4$ (0.1 mmol), $[Ln_2(O_2CtBu)_6(HO_2CtBu)_6]$ (0.075 mmol), and $H_2O_3PCH_2Ph$ (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 %.

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