

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

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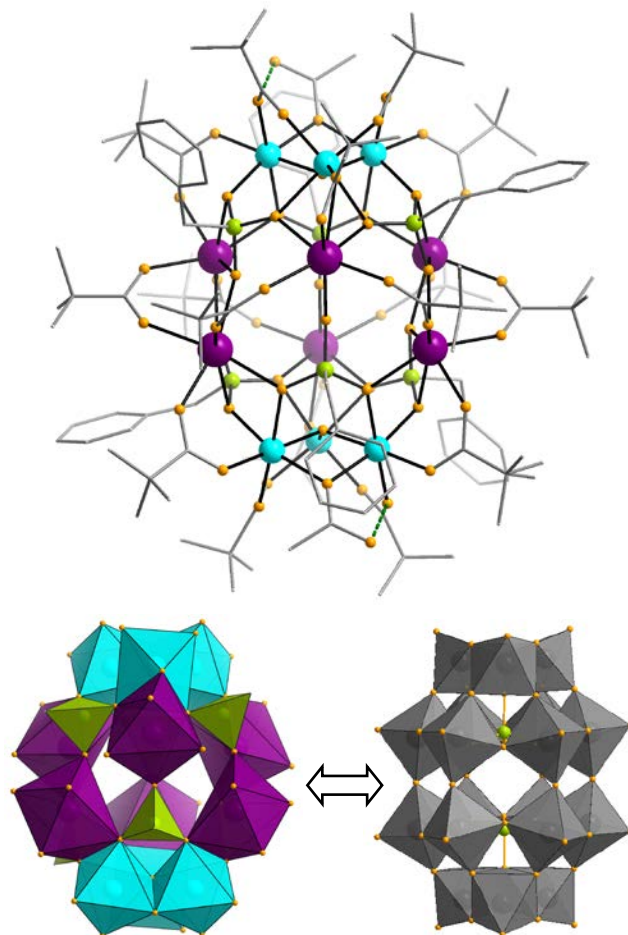
Magnetic refrigeration is based on the magnetocaloric effect (MCE) which relies on the entropy change of a material when placed in a magnetic field.<sup>1</sup> Molecular magnets have recently been examined in this context, especially high spin isotropic magnetic molecules.<sup>2-8</sup> The very large MCE observed for some of these cages suggests they could be used as a replacement for helium-3 in some applications; the expense and rarity of helium-3 makes this worth further investigation.

Recently, paramagnetic metal ions have been used as vertices in high-symmetry cages such as the Keplerate,<sup>9</sup> and this has led to the observation of exotic magnetic phenomena associated with the perfect spin-frustrated topology.<sup>10</sup> Moreover, such a geometrically frustrated pattern enhances the field dependence of the MCE due to the increased number of populated spin states.<sup>2,11</sup> Phosphonate as a tridentate ligand has its potential to form spherical cages due to the appropriate O-P-O angles (usually between  $100^\circ$  and  $120^\circ$  when coordinated).<sup>12</sup> We have been able to use it to construct cobalt-gadolinium grid-like complexes,<sup>13</sup> in which the presence of four-coordinate cobalt(II) ions are vital in the formation of the planar-type structures rather than cages. We thought it worth investigating similar chemistry with nickel(II).

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

Compounds **1-3** crystallise in the same space group  $P2_1/n$ . Since they are isomorphous we will describe the structure of **1** only. The crystal structure of **1** features a centrosymmetric rugby-ball shaped core (Figure 1).<sup>17</sup> The two ends of the rugby ball are capped by a  $\{\text{Ni}_3(\mu_3\text{-OH})\}$  triangle, in which the  $\mu_3\text{-OH}$  group is displaced by *ca.* 0.48 Å out of the  $\text{Ni}_3$  plane. There are two 2.11<sup>18</sup> pivalates and one

2.20 acetate ligands that bridge the edges of these  $\{\text{Ni}_3(\mu_3\text{-OH})\}$  triangles (see also Figure S1 in supporting information).



**Figure 1.** Upper: the structure of **1-3** in the crystal. Colour codes: Ln, purple; Ni, cyan; P, green; O, orange; C, grey. Hydrogen bondings are illustrated with dotted green line. Lower: polyhedral representation of the cores (left) and the Wells-Dawson ions (right).

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[\*\*] REPW...YZZ is grateful for the support of Marie Curie International Incoming Fellowship (EC Contract No: PIIF-GA-2008-219588). ME acknowledges the MICINN for contracts MAT2009-13977-C03 and CSD2007-00010.

The presence of the  $\mu$ -acetato-*O* makes one edge of the  $\text{Ni}_3$  triangle is significantly 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). Since the starting materials have no acetate the presence of the acetate is probably from the hydrolysis of the acetonitrile during solvothermal synthetic condition, which has been previously observed.<sup>19</sup> The coordination geometry of the inner side of the  $\{\text{Ni}_3\}$  triangles are completed by oxygen atoms from three phosphonates and three pivalates. The phosphonates adopt either 5.222 or 5.221 coordination mode binding 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  $\text{Ni}\cdots\text{Gd}$  separation of either 3.50 Å or 3.24 Å, respectively. The alternating arrangement of the Gd and the P atoms forms a  $\text{Gd}_3\text{P}_3$  six-member ring, which connects to its centrosymmetric-



related counterpart in an offset way with the aid of six peripheral 2.11 pivalates. The Gd...Gd separations within the Gd<sub>3</sub>P<sub>3</sub> six-member ring are around 6.2 Å, whereas between the Gd<sub>3</sub>P<sub>3</sub> six-member ring are in the range of 3.9-4.9 Å. Interestingly, if the P atoms are counted in the core of **1** is exactly an eighteen-member (Ni<sub>6</sub>Ln<sub>6</sub>P<sub>6</sub>) cage that resembles the Wells-Dawson polyoxometallate, as shown by the polyhedral picture in the bottom of Figure 1. This compliments the paramagnetic “Keggin” ions that have recently been reported.<sup>20</sup>

The magnetic behaviour 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 expected value: for **1**, observed 55.3 emu K mol<sup>-1</sup> (*calc.* 54.1 emu K mol<sup>-1</sup> for six  $S = 1$ ,  $g = 2.2$  and six  $S = 7/2$ ,  $g = 1.99$  centres); for **2**, observed 93.6 emu K mol<sup>-1</sup> (*calc.* 92.3 emu K mol<sup>-1</sup> for six  $S = 1$ ,  $g = 2.2$  and six  $S = 5/2$ ,  $L = 5$ ,  $g = 4/3$ , centres); for **3**, observed 7.9 emu K mol<sup>-1</sup> (*calc.* 7.3 emu K mol<sup>-1</sup> for six  $S = 1$ ,  $g = 2.2$  centres). In each case the difference suggests ferromagnetic exchange may be present.

Upon cooling, for **1**,  $\chi T$  remains steady down to 100 K before it increases gradually to a maximum around 57.0 emu K mol<sup>-1</sup> at 14 K. Below this temperature  $\chi T$  turns downward to a minimum of 46.1 emu K mol<sup>-1</sup> at 2 K. Magnetization measurements on **1** at low temperatures (2 to 10 K) were also performed (insert of the upper figure in Figure 2). The magnetization ( $M$ ) reaches 55.3  $\mu_B$  at 7 T at 2 K, which is the exact expected saturated value considering six  $S = 1$ ,  $g = 2.25$  and six  $S = 7/2$ ,  $g = 1.99$  centres. For **2**,  $\chi T$  vs.  $T$  curve decreases significantly with  $T$  to a minimum of 85.4 emu K mol<sup>-1</sup> at 12 K before it increases to a value of 85.9 emu K mol<sup>-1</sup> at 7 K. The decrease of  $\chi T$  at higher temperature region is associated with the crystal field effect of the Dy(III) ion.<sup>21</sup> The  $M$  vs.  $H$  plots from 2 to 7 K (insert of middle figure in Figure 2) show a steady increase that reaches 45.3  $\mu_B$  at 7 T at 2 K without saturation. The rise at low temperature for **1** and **2** suggests that some exchange interaction present is probably ferromagnetic.

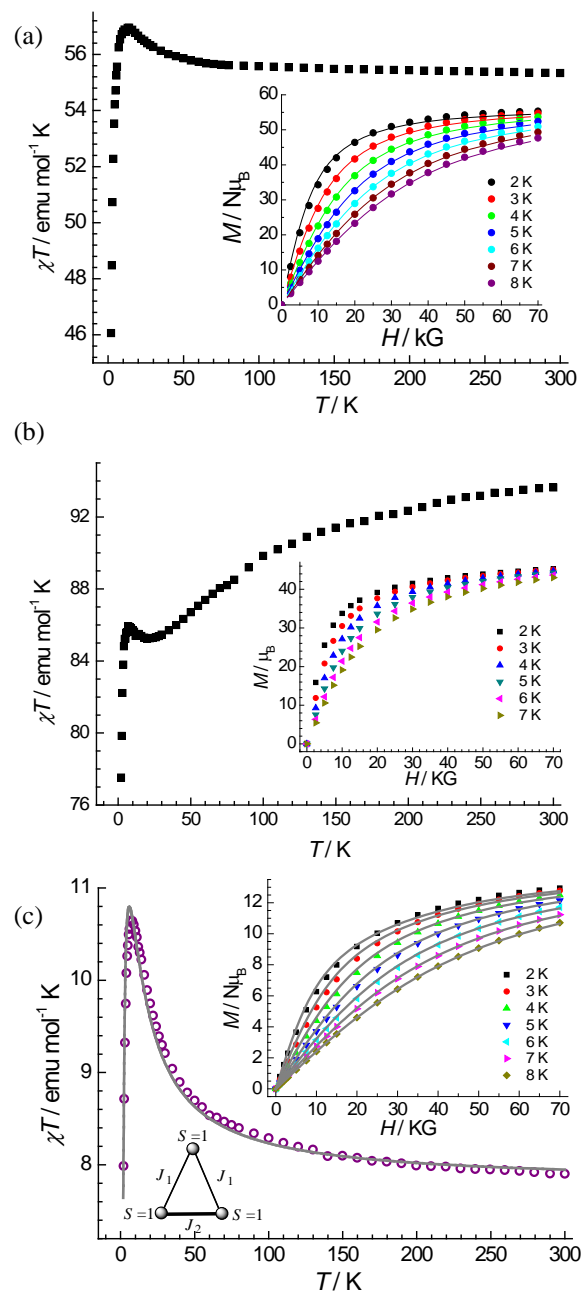
The magnetic study of compound **3** allows us to study the magnetic interactions between the nickel centres. The  $\chi T$  product of **3** raises gradually to a maximum of 10.6 emu K mol<sup>-1</sup> at 8 K before it sharply decreases to 8.0 emu K mol<sup>-1</sup> at 2 K. The whole plot as well as the magnetization plots can be modelled by program MAGPACK<sup>22</sup> using the following Hamiltonian (assuming there are two non-interacted Ni<sub>3</sub> triangles, see the coupling scheme inserted in the bottom figure of Figure 2 as well),

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

in which assumes that all the individual anisotropic parameters ( $D$  and  $g$ ) are the same. The best simulation (as indicated by the solid line in the bottom figure of Figure 2) gives  $J_1 = 2.83$  cm<sup>-1</sup>,  $J_2 = -1.18$  cm<sup>-1</sup>,  $D = 5.7$  cm<sup>-1</sup>, and  $g = 2.28$ . This model gives unequal magnetic interactions with the {Ni<sub>3</sub>} triangle. Dominated ferromagnetic exchange interaction is consistent with the rising of  $\chi T$  product at low temperature. A large  $D$  value of the individual Ni(II) ion, particularly compared to the  $J$  values, might indicate a non-well isolated ground spin state (the simulating result indicates a first excited energy level lying just ca. 3.0 cm<sup>-1</sup> above the ground state).

The magnetic data suggest that the lanthanide ions are only very weakly coupled to the two {Ni<sub>3</sub>} triangles. This is easily demonstrated by the fact that the magnetization of **1** can be very well reproduced by adding a Brillouin curve for each of the six Gd(III) ions to the magnetization of **3**, viz. the two {Ni<sub>3</sub>} triangles

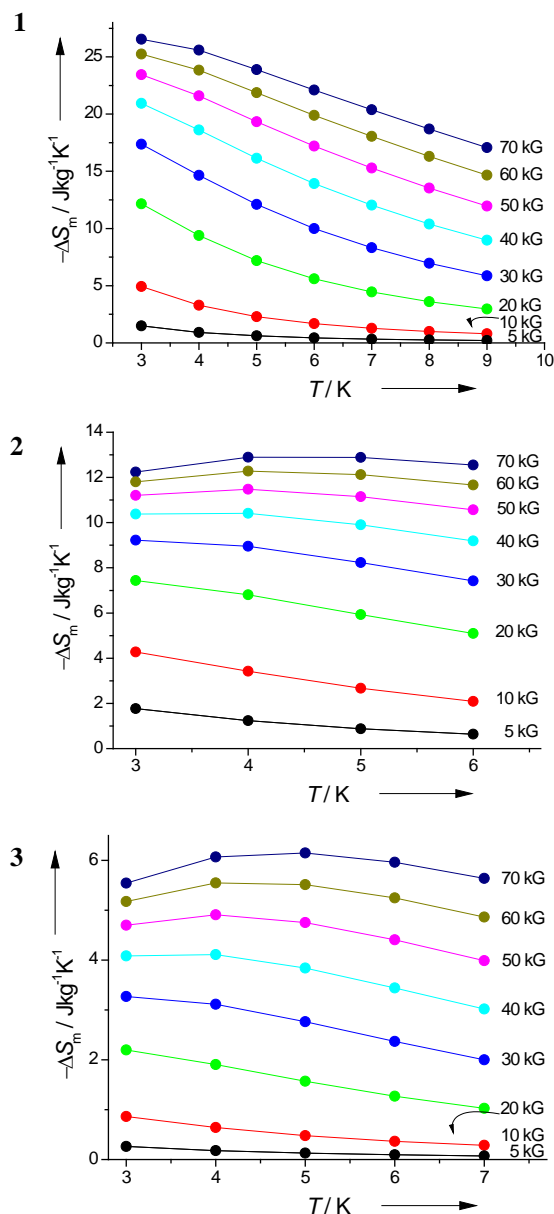
(Figure 2). In spite of the so-obtained excellent agreement, some weak antiferromagnetic correlation of type Ni(II)-Ln(III) or Ln(III)-Ln(III) should likely be present as suggested by the sudden drop of the experimental  $\chi T$  for **1** at the lowest temperatures.



**Figure 2.** The  $\chi T$  vs.  $T$  plot of **1** under 5 kG dc field (a). 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**. The  $\chi T$  vs.  $T$  plot of **2** under 1 kG dc field (b). Inset: the field-dependent magnetization plots at indicated temperatures. The  $\chi T$  vs.  $T$  plot of **3** under 5 kG dc field (c). Inset: the field-dependent magnetization plots at indicated temperatures (upper) and the coupling scheme used for simulation (lower). Solid grey lines in (c): simulation curve by using the model described in the text.

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 within the investigated temperature range. The large values for the magnetization make these possible candidates for low temperature magnetic cooling, as the MCE can be described as

$\Delta S(T)\Delta H = \int [\partial M(T,H)/\partial T]_H dH$ .<sup>1,6</sup> Calculating the magnetic entropy changes obtained from the magnetisation 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<sup>-1</sup> K<sup>-1</sup>. The entropy change of **1** is much larger than the value reported for the 3d-4f compounds at 4 K.<sup>5,13</sup> and even slightly higher than the highest value reported (25 J kg<sup>-1</sup> K<sup>-1</sup>), for a {Mn<sub>14</sub>} cage.<sup>3b</sup> It is noticeable that the smallest MCE is found for **3**, which indicates the much larger entropy changes in **1** and **2** are mainly attributed to the lanthanide ions with more unpaired electrons.<sup>5</sup>



**Figure 3.** Experimental magnetic entropy changes  $\Delta S_m$  for **1-3**, obtained from the magnetization data, at various fields and temperatures. Lines are guides to the eye.

The maximum entropy value per mole involved, corresponding to  $n = 6$  Ni(II) spins  $s = 1$  and, eventually, 6 Dy(III) spins  $s = 5/2$  or 6 Gd(III) spins  $s = 7/2$  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<sup>-1</sup> K<sup>-1</sup>, for **1**, **2** and **3**, respectively. These values are not reached experimentally

because of the anisotropy combined with the magnetic correlations.<sup>8</sup> The same simple model of non-interacting {Ni<sub>3</sub>} triangles and lanthanide ions can again be used to interpret the observed magnetic entropy changes. For **3**, assuming e.g. full ferromagnetic order within each {Ni<sub>3</sub>} triangle, one would expect the maximum entropy to not exceed  $2R \ln(7) = 3.9R = 8.4$  J kg<sup>-1</sup> K<sup>-1</sup>. To experimentally reach this value, a field somewhat larger than 70 kG is needed to overcome the anisotropy of the Ni(II) ions (Figure 3). Replacing yttrium with gadolinium results in an added magnetic entropy of  $6R \ln(8)$ , for which the maximum entropy value of **3** amounts to  $16.4R = 32.0$  J kg<sup>-1</sup> K<sup>-1</sup>. The magnetic isotropy of the Gd(III) ions, combined with the negligible Gd(III)-Gd(III) and Gd(III)-Ni(II) interactions, permits that the experimental  $-\Delta S_m$  reaches a value close to this limiting value for  $\Delta H = 70$  kG. As shown in Figure 3, this field strength is far from sufficient in case a large anisotropy gets involved as for **2**, for which the added entropy of  $6R \ln(6)$  results in a maximum entropy of  $14.6R = 28.4$  J kg<sup>-1</sup> K<sup>-1</sup>. The effect of increasing the anisotropy is not only that of inhibiting the achievement of relatively large  $-\Delta S_m$  values. By comparing the temperature dependencies of the magnetic entropy change for **1** and **2**, one can notice the expected behaviour, i.e. the maximum shifts to higher temperature for the anisotropic complex.<sup>8</sup>

In summary, by using phosphonates, we have successfully synthesized a series of molecular cages which can be described as Wells-Dawson analogues. The gadolinium analogue of this series of compounds shows huge MCE at low temperatures. This is the result of the magnetic isotropy combined with negligible interactions involving the Gd(III) ions, leading to a large number of populated paramagnetic states even at low temperature. Gadolinium is often used in magnetic refrigerants;<sup>1</sup> these results and those from the Brechin group,<sup>5</sup> suggest that polymetallic Gd cages could have significant utility in low temperature cooling. While there has been a great deal of recent work using phosphonates to make paramagnetic cages,<sup>23</sup> 3d-4f heterometallic cages reported using these ligands remain unusual.<sup>13,24,25</sup>

## Experimental Section

See supporting information

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

**Keywords:** molecular · magnetic · refrigerant · phosphonate · 3d-4f

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