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## Single Molecule Magnet behaviour in a $\{Dy_4P_2\}$ Octahedron

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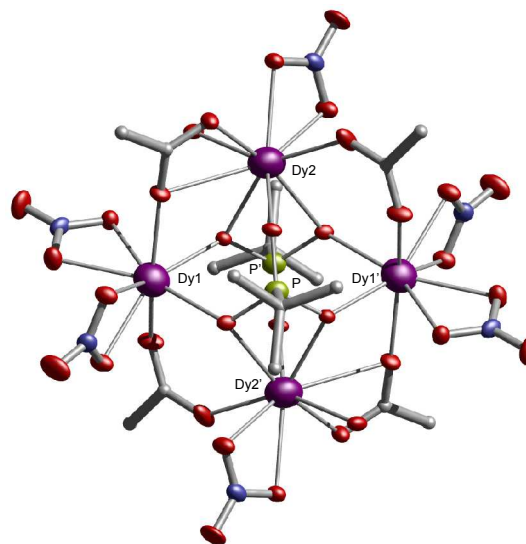
**Two new tetrametallic lanthanide-phosphonate complexes have been structurally and magnetically characterised. The  $\{Dy_4\}$  complex is a single molecule magnet.**

Organophosphonates  $[RP(O)_2OH]^-$  and  $[RPO_3]^{2-}$ , obtained from the deprotonation of  $[RP(O)(OH)_2]$ , are ideal for assembly of cage compounds.<sup>1-3</sup> We have been studying these ligands as routes to cages involving lanthanides, including mixed-metal 3d-4f cages.<sup>4,5</sup> The possible applications of such cages are dependent on the 4f-ions; where the isotropic ion Gd(III) is involved most studies target magnetic cooling through the magnetocaloric effect (MCE).<sup>6</sup> When the anisotropic ion Dy(III) is employed, the blockage of the relaxation of the magnetisation is often observed, leading to single molecule magnets (SMMs),<sup>7</sup> which have been proposed for application in information storage and processing.<sup>8</sup>

In principle, a single phosphonate ligand can bind to as many as nine metal centres; this can create problems especially for metal ions with high coordination numbers. Lanthanide phosphonates often have poor solubility due to a propensity to form coordination polymers, and this can make them difficult to characterise.<sup>9</sup> We have circumvented this problem with a variety of strategies, and demonstrated that discrete molecules containing lanthanides and phosphonates, such as  $\{Ln_4P_4\}^{5a}$ ,  $\{Ln_8P_6\}^{5b}$  and  $\{Ln_{10}P_6\}^{5c}$  can be obtained. These cages besides having aesthetically pleasant structures also show some potential for magnetocaloric applications when Ln = Gd(III).<sup>5,6</sup>

Homometallic lanthanide phosphonate cages remain rare. Here we report the synthesis and magnetic properties of two further Ln–phosphonate cages (Ln = Gd(III), **1** and Dy(III), **2**)

formed using *t*-butylphosphonate, The compounds have the general formula  $[Ln_4(O_3P^tBu)_2(O_2C^tBu)_4(NO_3)_6(H_2O)_2]^{2-}$  (Figure 1 and S1). Compound **2** shows slow relaxation of magnetisation.



**Figure 1.** Crystal structure of  $[Dy_4(O_3P^tBu)_2(O_2C^tBu)_4(NO_3)_6(H_2O)_2]^{2-}$ . Colour code: Dy, purple; P, green; N, blue; O, red; C, grey; H omitted for clarity.

We have previously studied the reaction of  $[Ln_2(O_2C^tBu)_6(HO_2C^tBu)_6]$  with oxo-centred metal triangles  $[M_3(\mu_3-O)(O_2C^tBu)_6(py)_3](O_2C^tBu)$  in the presence of  $H_2O_3P^tBu$  and pyridine.<sup>5c,10</sup> When M = Cr(III) we find formation of  $\{Cr_6Ln_2\}$  cages,<sup>10</sup> but with M = Co(III) we find the triangle is inert, and merely acts as cation with the phosphonate reacting with the lanthanide to form anionic  $\{Ln_{10}P_6\}$  centred-rings.<sup>5c</sup>

The reaction depends on the lanthanide precursor. Here, the same general procedure was followed that produces the  $\{Ln_{10}P_6\}$  rings,<sup>5c</sup> but hydrated lanthanide nitrates were used as the precursor, thus significantly reducing the availability of pivalate as a ligand. After heating for 7h light-brown crystals formed over three weeks at room temperature in yields of 20–

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25%. X-ray studies show a salt of formula  $[\text{Co}_3(\mu_3\text{-O})(\text{O}_2\text{C}^t\text{Bu})_6(\text{py})_3]_2[\text{Ln}_4(\text{O}_3\text{P}^t\text{Bu})_2(\text{O}_2\text{C}^t\text{Bu})_4(\text{NO}_3)_6(\text{H}_2\text{O})_2]$  ( $\text{Ln} = \text{Gd(III)}$ , **1** and  $\text{Dy(III)}$ , **2**) (Figure 1 and S1) has formed.

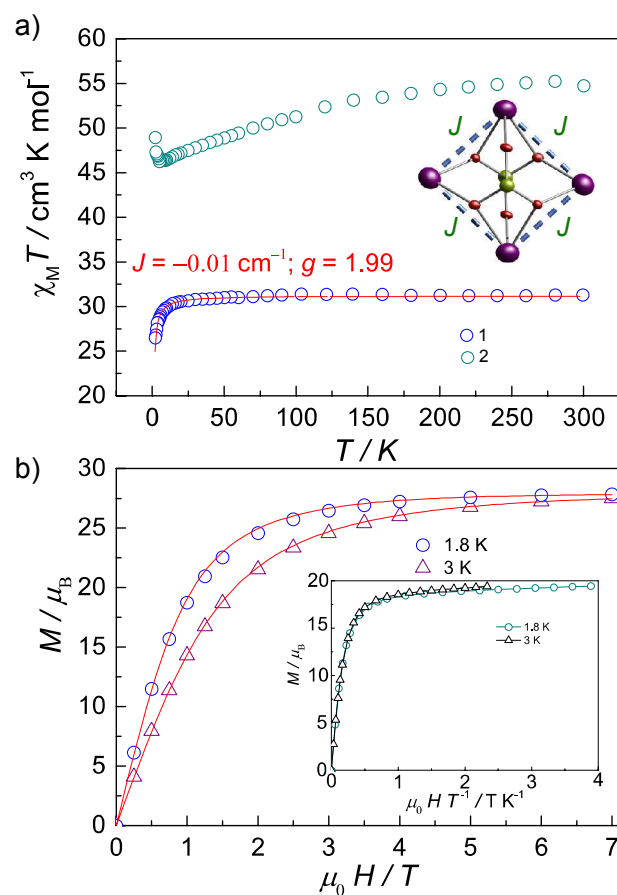
The compounds **1** and **2** are isostructural, and crystallise in the monoclinic space group  $P2_1/n$ . They contain an anionic  $\{\text{Ln}_4\}^{2-}$  cage with two  $[\text{Co}_3(\mu_3\text{-O})(\text{O}_2\text{C}^t\text{Bu})_6(\text{py})_3]^+$  cations (Figure S1). We describe the dysprosium-containing compound **2** as representative. The anion is on an inversion centre and contains four Dy(III) metal ions, two phosphonates, six nitrates, four pivalates and two terminal water molecules. The metal ions along with the phosphorous centres can be described as a tetragonally distorted octahedron (Figure 1). The four Dy(III) atoms (Dy(1), Dy(2), Dy(1') and Dy(2')) lie in a single plane and form a distorted rectangle (Dy(1)–Dy(2) = 3.965(5), Dy(1)–Dy(2') = 4.203(8) Å, Dy(2')–Dy(1)–Dy(2) = 85.91(4), Dy(1')–Dy(2)–Dy(1) = 94.09(5)°). The two phosphorous atoms P and P' from the phosphonates are in trans-sites of an octahedron; the phosphonates bind using the 4.221 coordination mode (Harris notation)<sup>11</sup> (Figure 1). The P...P' distance within the distorted octahedron is 3.717(3) Å.

The metal centre Dy(1) is bound to two 2.110-nitrates while Dy(2) is bound to one such nitrate ligand and one terminal water molecule. The Dy...Dy edges within the parallelogram are bridged by four pivalates, two of them adopting 2.11 coordination mode and the other two adopting 2.21 coordination mode. The Dy(1) site is eight coordinate with a triangular dodecahedral geometry ( $D_{2d}$ ) (with a Continuous Shape Measure value (CSHM) of 2.745).<sup>12</sup> The Dy(2) site is nine coordinate with a less regular geometry, described as a muffin (Cs, with a CSHM value of 3.265)<sup>12</sup> (Table S1 and Figure S2).

The magnetic properties of both systems have been studied in the temperature range of 2–300 K under an applied DC field of 1 kOe. For **1** the product  $\chi_M T$  (being  $\chi_M$  the molar magnetic susceptibility) shows an expected room temperature value of 31.3 cm<sup>3</sup> mol<sup>-1</sup> (Calcd. 31.2 cm<sup>3</sup> K mol<sup>-1</sup>, for four Gd(III);  $g = 1.99$ ,  $S = 7/2$ ). Upon cooling  $\chi_M T$  stays practically constant down to ca. 15 K where it decreases to 26.5 cm<sup>3</sup> K mol<sup>-1</sup> (at 2 K) (Figure 2a) indicating weak antiferromagnetic interactions. The molar magnetisation ( $M_B$ ) at 1.8 and 3 K saturates at 28  $\mu_B$  above ca. 5 T (Figure 2b). The exchange interaction in **1** can easily be obtained through simultaneous fitting of  $\chi_M T(T)$  and  $M_B(H)$  to a Hamiltonian of the form:  $H = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_1\hat{S}_4) + g\mu_B H \sum_{i=1}^4 \hat{S}_i$  (see inset Figure 2a) using the program PHI.<sup>13</sup> This gives a single exchange interaction,  $J = -0.01$  cm<sup>-1</sup>. This very small interaction is of the order of the zero-field splitting of Gd(III) ions, and we cannot exclude the possibility that this fall is a purely single ion effect.

The room temperature  $\chi_M T$  for **2** similarly is in good agreement with the expected value for four non-interacting Dy(III) ions 55.2 cm<sup>3</sup> K mol<sup>-1</sup> (Calcd. 56.6 cm<sup>3</sup> K mol<sup>-1</sup>, for four Dy(III), ground state  $^6\text{H}_{15/2}$ ,  $g_J = 4/3$ ,  $J = 15/2$ ). Upon cooling  $\chi_M T$  slowly decreases to a minimum of 46.2 cm<sup>3</sup> K mol<sup>-1</sup> at about 5 K due to depopulation of the Stark levels<sup>14</sup> before increasing again at lower temperatures to a maximum of 48.9 cm<sup>3</sup> K mol<sup>-1</sup>. This suggests a weak ferromagnetic interaction between the Dy centres (Figure 2a). Interestingly, the  $M_B(H)$  for **2** rapidly

increases upon application of the magnetic field leading to a saturation value of 19  $\mu_B$  at ca. 5 T (see inset Figure 2b).

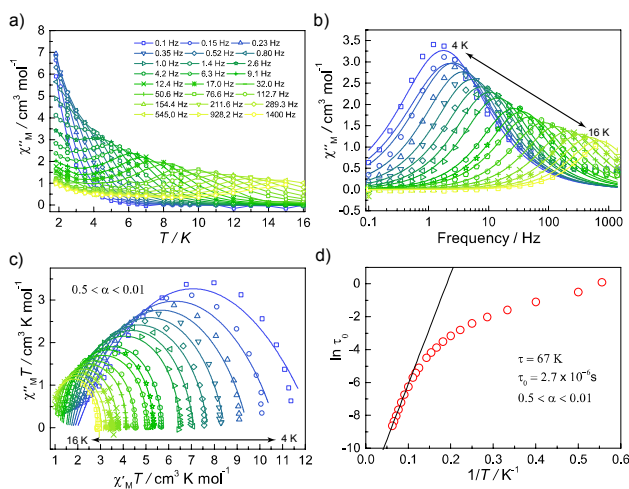


**Figure 2.** (a) Variation of  $\chi_M T$  vs.  $T$  for **1** and **2** at 1 kOe from 2–300 K; (b)  $M_B$  vs.  $H$  for **1** and simulations (solid red lines) and reduced magnetisation for compound **2** (inset) from 0–7 T at 2 and 4 K and (solid lines in inset are guides to the eye).

The dynamic magnetic behaviour of **2** was investigated by alternating current (ac) susceptibility measurements as a function of temperature (2–16 K) and frequency ( $\nu = 0.1 - 1400$  Hz) (Figure 3). Ac measurements of **2** show a frequency dependent behaviour, which is further improved by the application of a small-applied dc field, which reduces fast quantum tunnelling. Under an optimal field of 0.6 kG both the in-phase ( $\chi'_M$ ) and out-of-phase ( $\chi''_M$ ) susceptibility shows frequency dependence below 16 K, characteristic of SMMs (Figure 3a,b and S3).

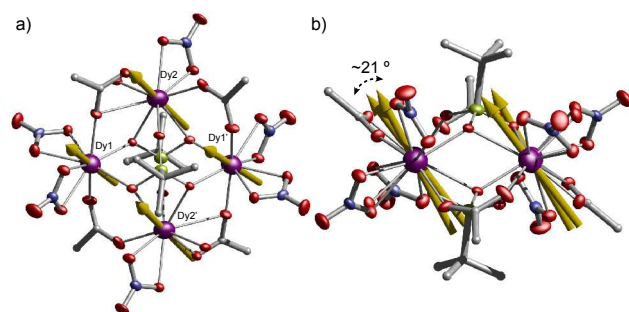
A single frequency dependent peak is observed in the  $\chi'_M(T)$  and  $\chi''_M(T)$ , which becomes broader at lower temperatures. The  $\chi''_M(T)$  shows a maximum at 15 K for the highest measurement frequency ( $\nu$ ) of 1.4 kHz. The peaks in  $\chi''_M(\nu)$  show a linear dependence on temperature above 11 K, and can be described using the Arrhenius law (Figure 3d), giving a thermal energy barrier to magnetisation relaxation  $U_{\text{eff}} = 67$  K with  $\tau_0 = 2.7 \times 10^{-6}$  s (Figure 3d). Cole-Cole plots ( $\chi'_M$  vs.  $\chi''_M$ ) for the temperature range 4 – 9.5 K give temperature-dependent  $\alpha$  parameters: at high temperatures  $\alpha = 0.05$ ,

characteristic of a single relaxation time. Below 11 K the peaks show a non-linear dependence on temperature, indicating non-Orbach relaxation processes are becoming important; the  $\alpha$  value increases to 0.50, also suggesting multiple relaxation processes are operative (Figure 3c).



**Figure 3.** (a)  $\chi''_M(T)$ , (b)  $\chi''_M(\nu)$ , (c) Cole-Cole plot and simulations (solid lines) and (d) Arrhenius analysis for **2** at 0.6 kOe.

The slow relaxation of the magnetisation observed in Dy(III) complexes is due to a well-defined  $m_j = \pm 15/2$  ground state doublet and highly axial  $g$ -tensors (ideally  $g_x = g_y = 0$ ;  $g_z = 20$ ) of the  ${}^6H_{15/2}$  manifold. Taking into account the ligand set surrounding the two Dy(III) sites in **2**, and employing an electrostatic method<sup>15</sup> based upon electrostatic minimisation of  $\rho_{\pm 15/2}^{(\alpha,\beta)}$  Sievers electron density<sup>16</sup> and a minimal valence bond model we have been able to predict the directionality of the magnetic axes in **2**, resulting in an almost collinear arrangement with a deviation between magnetic axes of  $21^\circ$  (Figure 4). The almost parallel arrangement of the axes is in good agreement with the dynamic magnetic behaviour, since non-collinear magnetic arrangement and small exchange interactions tend to accelerate the quantum tunnelling through further relaxation pathways.<sup>17</sup>



**Figure 4.** Magnetic axes obtained through electrostatic method (yellow arrows) (a) top and (b) side view for compound **2**. Colour code: same than in Figure 1.

In summary, by using phosphonates, we have successfully synthesised two isostructural molecular cages, the metal core

consists of four Ln(III) ions which are arranged at the vertices of a parallelogram. While there has been a great deal of recent work to make paramagnetic phosphonate cages,<sup>1</sup> compound **2** appears to be the first homometallic 4f-phosphonate cages with SMM behaviour.

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## Notes and references

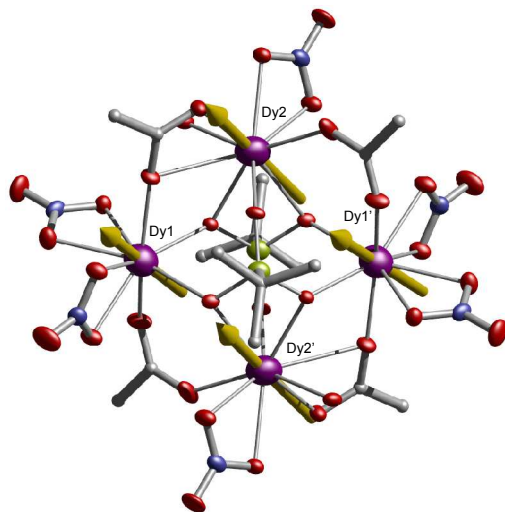
‡ Crystal data for **1** [ $C_{122}H_{202}Co_6Gd_4N_{14}O_{60}P_2$ ]:  $M_r = 3869.48$ , monoclinic, space group  $P2_1/n$ ,  $T = 128.1(4)$  K,  $a = 11.7554(2)$ ,  $b = 19.4689(4)$ ,  $c = 36.4118(7)$  Å,  $\beta = 97.9131(17)^\circ$ ,  $V = 8254.0(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.557$  g cm<sup>-3</sup>, total data = 64303,  $R_1 = 0.0479$  for  $I \geq 2\sigma$  (I) and  $wR_2 = 0.0670$ ; Crystal data for **2** [ $C_{122}H_{202}Co_6Dy_4N_{14}O_{60}P_2$ ]:  $M_r = 3890.48$ , monoclinic, space group  $P2_1/n$ ,  $T = 150.0(1)$  K,  $a = 11.7542(2)$ ,  $b = 19.4585(19)$ ,  $c = 36.4590(7)$  Å,  $\beta = 97.9842(19)^\circ$ ,  $V = 8258.0(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.565$  g cm<sup>-3</sup>, total data = 41706,  $R_1 = 0.0448$  for  $I \geq 2\sigma$  (I) and  $wR_2 = 0.0900$ . The data were collected on an Agilent SuperNova CCD diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å), solved using SUPERFLIP<sup>18a</sup>, and refined on  $F^2$  using SHELX-14<sup>18b</sup> in Olex2.<sup>18c</sup>

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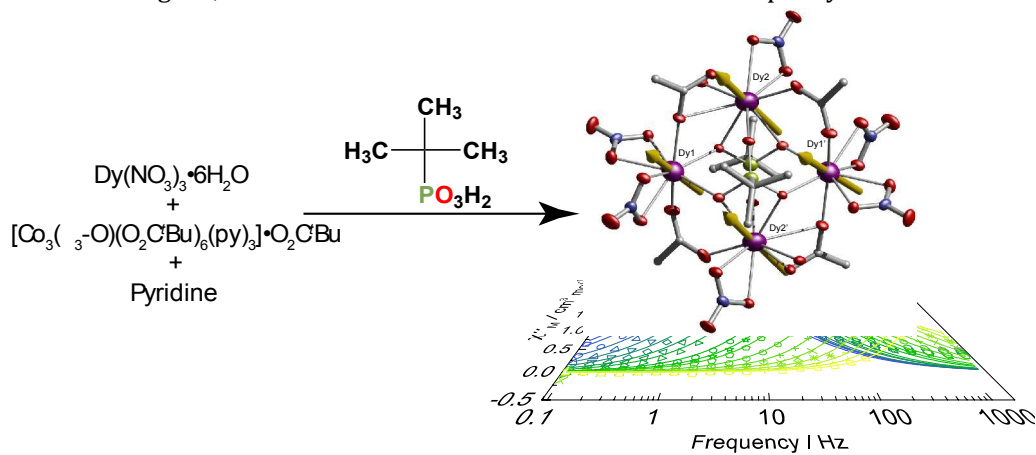


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Two new {Ln<sub>4</sub>} cages are reported, bridged by phosphonate ligands. The anisotropy axes at the Dy(III) sites are aligned, leading to slow relaxation of magnetisation.