

## Centred nine-metal rings of lanthanides†

Cite this: DOI: 10.1039/c3cc48708c

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Accepted 12th December 2013

DOI: 10.1039/c3cc48708c

www.rsc.org/chemcomm

**Two {Ln<sub>10</sub>} cages are reported (Ln = Dy or Gd) which feature a nine-metal ring surrounding a central metal site. Magnetic studies show weak anti-ferromagnetic exchange around the nine-metal ring, which should create spin frustration.**

Cyclic metal cages fall into two broad families. In one family the metal sites are confined to the rim of the cage forming a metal ring, where the metals can be single metal sites<sup>1</sup> or metal cages.<sup>2</sup> In the second family there is a metal at the centre of the cage, and these are called either metallocrowns<sup>3</sup> or metallo-coronands.<sup>4</sup> Both classes have been studied, the former largely because of they can act as model compounds for studying physical phenomena, especially in magnetic molecules.<sup>1</sup> For metallocrowns studies extend to selective ion binding, as well as studies of interesting magnetic behaviour.<sup>5</sup> For both families most examples involve 3d-metal ions, although there are remarkable polymolybdate<sup>2a</sup> and palladium phosphonate rings.<sup>2c</sup> Several metal rings have been reported for the 4f-metals,<sup>6</sup> and for 3d–4f cages,<sup>7</sup> but many fewer centred cyclic structures.<sup>8</sup> Most rings and metallocrowns contain an even-number of metal sites in the cyclic portion, although metallocrowns are known with three<sup>9</sup> or five<sup>10</sup> metals in the backbone. Few large odd-numbered rings have been reported.<sup>11</sup> Here we report two cyclic {Ln<sub>10</sub>} cages (Ln = Dy, **1** or Gd, **2**), where there is a nine-metal ring centred by a tenth metal site.

To synthesise 4f-phosphonate cages we have used pivalate as a co-ligand,<sup>12</sup> and we have reported a number of Co-4f cages.<sup>13</sup> We were intending to extend this work by reacting [Ln<sub>2</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>6</sub>-(HO<sub>2</sub>C<sup>t</sup>Bu)<sub>6</sub>] (Ln = Dy and Gd) with [Co<sub>3</sub>(μ<sub>3</sub>-O)(O<sub>2</sub>C<sup>t</sup>Bu)<sub>6</sub>(py)<sub>3</sub>]<sup>-</sup>(O<sub>2</sub>C<sup>t</sup>Bu), H<sub>2</sub>O<sub>3</sub>P<sup>t</sup>Bu and pyridine; the Co<sup>III</sup> cage was used to try to

control reactivity by using an inert 3d-metal and hence achieve a more predictable cage than using Co<sup>II</sup> substrates.<sup>13</sup> After heating for seven hours, light-brown crystals form over two weeks at room temperature in yields of 10–20% based on lanthanide pivalate. X-ray studies show formation of [Co<sub>3</sub>(μ<sub>3</sub>-O)(O<sub>2</sub>C<sup>t</sup>Bu)<sub>6</sub>(py)<sub>3</sub>][Ln<sub>10</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>18</sub>-(O<sub>3</sub>P<sup>t</sup>Bu)<sub>6</sub>(OH)(H<sub>2</sub>O)<sub>4</sub>] (Ln = Dy **1**, Gd **2**) (Fig. 1).‡ The compounds are isostructural, and contain an anionic {Ln<sub>10</sub>} cage co-crystallised with a [Co<sub>3</sub>(μ<sub>3</sub>-O)(O<sub>2</sub>C<sup>t</sup>Bu)<sub>6</sub>(py)<sub>3</sub>]<sup>+</sup> cation (Fig. S1, ESI†). We describe compound **1** as crystals of **2** do not diffract sufficiently well to allow a full structure determination.

The anion of **1** contains nine Dy<sup>III</sup> metal ions in a ring and a tenth Dy<sup>III</sup> metal ion at the centre of the structure (Fig. 1). Oxygen donors occupy all the coordination sites on these ten metals. The ten metal sites are almost co-planar; the mean deviation from the plane is 0.23 Å, with the maximum deviation of 0.43 Å found for the central metal site. The nine Dy<sup>III</sup> metal ions in the ring are arranged at the vertices of an approximately regular nonagon (or enneagon). The distances from the central Dy (Dy10) to the rim fall into two groups; there are longer contacts to Dy2, Dy5 and Dy8,

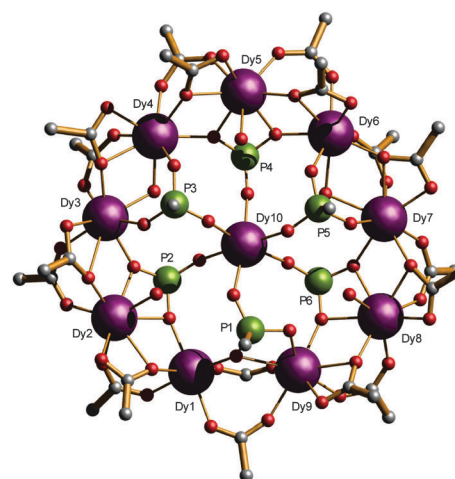


Fig. 1 Crystal structure of **1**. Colours: Dy, purple; P, green; O, red; C, grey. H-atoms and Me groups omitted for clarity.

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† Electronic supplementary information (ESI) available: Synthetic method, crystallographic details, crystallographic figures and magnetic information. CCDC 972030. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc48708c

averaging  $5.92 \pm 0.13 \text{ \AA}$ , while the remaining six contacts average  $5.47 \pm 0.12 \text{ \AA}$ . Eight of the distances between neighbouring Dy centres around the ring average  $3.83 \pm 0.13 \text{ \AA}$ ; the ninth contact (Dy1...Dy9) is longer at  $4.1496(2) \text{ \AA}$ .

Three of the six phosphonates lie below the plane of the  $\{\text{Dy}_{10}\}$  disc (P2, P4, P6) and adopt the 4.221 binding mode (Harris notation<sup>14</sup>); it is noticeable that these phosphonates chelate to the Dy sites that have the long contacts to the central dysprosium. The remaining three phosphonates are above the plane of metal centres; two (P3 and P5) adopt the 3.111 binding mode, while the third (P1) adopts 3.211 mode. This phosphonate removes the three-fold symmetry of the cage, and it is the Dy1–Dy9 edge bridged by a  $\mu_2$ -oxygen from this phosphonate that is the long Dy...Dy contact in the ring (see above). Each edge is also bridged by two pivalates, one with a 2.21 mode and the other with the 2.11 mode. The Dy3...Dy4 edge is bridged by a  $\mu$ -hydroxide (Dy–O distances of  $2.308(12)$  and  $2.294(11) \text{ \AA}$ ) while the Dy6...Dy7 is bridged by a  $\mu$ -water (Dy–O distances  $2.537(12)$  and  $2.635(12) \text{ \AA}$ ).

The central Dy10 site is six-coordinate, with a geometry approaching octahedral. The Dy–O distances range from  $2.207(10)$  to  $2.338(10) \text{ \AA}$ , with *cis* O–Dy–O angles between  $84.3(4)$  and  $98.4(4)^\circ$  while *trans* O–Dy–O angles like between  $171.6(4)$  and  $178.0(4)^\circ$ . Dy1 is also six-coordinate, bound to two O-donors from phosphonates and four from carboxylates. Dy2 to Dy8 are eight coordinate, bound to two phosphonate oxygens, five O-atoms from pivalates, and a further oxygen either from a terminal water, a bridging water or a bridging hydroxide. Dy9 is also eight coordinate bound to three phosphonate oxygens and five carboxylate oxygens. The oxo-centred  $[\text{Co}_3(\mu_3\text{-O})(\text{O}_2\text{C}^t\text{Bu})_6(\text{py})_3]^+$  cationic triangle features Co<sup>III</sup> sites around a central  $\mu_3$ -oxide (Fig. S1, ESI<sup>†</sup>). Each cobalt is bound to five O-donors, from the central oxide and 2.11 bridging pivalates (av. Co–O distance =  $1.89 \text{ \AA}$ ), with a terminal pyridine (av. Co–N distance =  $2.24 \text{ \AA}$ ).

Direct-current magnetic susceptibility studies of polycrystalline samples **1** and **2** were carried out in the temperature range 2–300 K (Fig. 2). At room temperature the value of the product  $\chi_M T$  (where  $\chi_M$  is the molar magnetic susceptibility) is  $135.0$  and  $78.5 \text{ emu K mol}^{-1}$  for **1** and **2** respectively. The value for **1** is close to that calculated for ten non-interacting ions, while that for **2** is slightly lower than that calculated for ten independent Gd<sup>III</sup> sites (calc.  $\chi_M T = 141.2 \text{ emu K mol}^{-1}$  for ten Dy<sup>III</sup> ions,  $^6\text{H}_{15/2}$ ,  $g = 4/3$ ; calc.  $\chi_M T = 77.9 \text{ emu K mol}^{-1}$  for ten Gd<sup>III</sup> ions,  $^8\text{S}_{7/2}$ ,  $g = 1.99$ ). For **1** the  $\chi_M T$  product gradually decreases until around 35 K and then decreases more rapidly. This behaviour is typical of Dy<sup>III</sup> complexes and is due to depopulation of the Stark sub-levels.<sup>15</sup> **1** does not show slow relaxation of magnetisation. For **2**,  $\chi_M T$  remains fairly constant to 20 K before falling. The  $M$  versus  $H/T$  data for **2** at low temperature show a rapid increase of magnetisation, reaching  $69.6 \mu_B$  at 7 T at 2 K, which is close to the saturation value for ten  $S = 7/2$  centres with  $g = 2.00$  ( $69.8 \mu_B$ , inset Fig. 2b). For **1**, the  $M$  versus  $H/T$  curve increases gradually with increasing field, reaching  $52.2 \mu_B$  at 7 T at 2 K without reaching saturation (Fig. S3, ESI<sup>†</sup>).

While it is presently impossible to model data for a  $\{\text{Dy}_{10}\}$  cage, for the isotropic  $\{\text{Gd}_{10}\}$  cage modern quasi approximate methods allow us to model the magnetic data, despite the

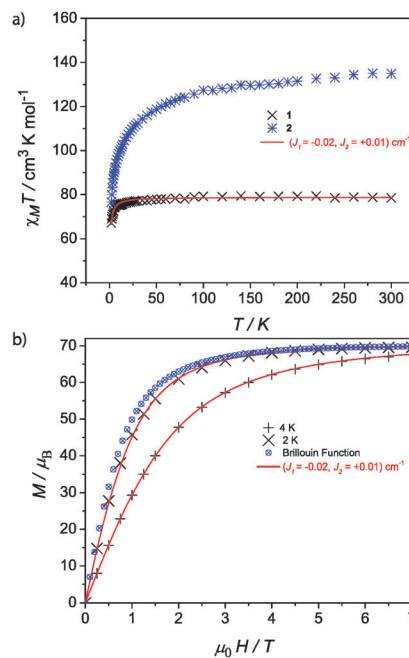


Fig. 2 (a) Variation of  $\chi_M T$  with  $T$  for **1** and **2** in a magnetic field of 1000 Oe in the temperature range 2 to 300 K; (b) magnetisation against field for **2** from 0–7 T at 2 and 4 K, simulation and Brillouin function for 10 non-interacting Gd<sup>III</sup> ions.

enormous Hilbert space of  $(2S + 1)^n$  where  $n = 10$  is the number of Gd centres; this yields 576650390625. We employ the Finite-Temperature Lanczos Method, which is a Krylov-space method and has proven to be very accurate.<sup>16</sup> We have chosen a Hamiltonian with one exchange interaction around the ring ( $J_1$ ), and a second between the central Gd ion and those in the ring ( $J_2$ ), *i.e.* assuming an approximate  $C_9$  symmetry:

$$\hat{H} = -2J_1 \left( \sum_{i=1}^8 \hat{s}_i \cdot \hat{s}_{i+1} + \hat{s}_1 \cdot \hat{s}_9 \right) - 2J_2 \sum_{i=1}^9 \hat{s}_i \cdot \hat{s}_{10} + g\mu_B B \hat{S}_z,$$

where  $\hat{s}_i$  denote individual spin operators at site  $i$  and  $\hat{S}_z$  denotes the  $z$ -component of the total spin operator. An excellent fit of the  $\chi_M T$  vs.  $T$  and  $M$  vs.  $H$  data could be obtained with several parameter sets, all with both  $J_1$  and  $J_2$  very small (see Fig. S2, ESI<sup>†</sup> for further simulations). The best parameters are  $J_1 = -0.02$ ,  $J_2 = +0.01 \text{ cm}^{-1}$ . These numbers are barely distinguishable from zero, however they would generate a highly frustrated magnetic system, with the nine Gd<sup>III</sup> ions around the ring unable to align mutually anti-parallel with their nearest neighbours. Unfortunately the extremely small exchange interactions mean that any interesting physics arising from frustration<sup>17</sup> could only be seen at temperatures below 100 mK.

The large magnetisation value obtained for **2** and negligible anisotropy of Gd<sup>III</sup> ( $^8\text{S}_{7/2}$ ) makes this cluster a good candidate for MCE applications (Fig. S3, ESI<sup>†</sup>). The magnetic entropy changes of **2** for changing applied field can be calculated by the Maxwell equation for magnetic entropy  $(\partial S_m / \partial H)_T = (\partial M(T, M) / \partial T)_H$  where the integration for an isothermal process yields  $\Delta S = \int [(\partial M(T, H) / \partial T)_H] dH$ .<sup>18</sup> This equation gives magnetic entropy

change for 2 at 3 K and for a field changes  $\Delta H = 0.5\text{--}7$  T which corresponds to  $28.5 \text{ J kg}^{-1} \text{ K}^{-1}$ . Much higher values have been reported for pure Gd-cages, for example  $46.1 \text{ J kg}^{-1} \text{ K}^{-1}$  for a  $\{\text{Gd}_{24}\}$  cage,<sup>19</sup> and for 3D Gd-frameworks, e.g.  $59 \text{ J kg}^{-1} \text{ K}^{-1}$  for  $[\text{Gd}(\text{O}_2\text{CH})_3]_n$ .<sup>20</sup> The smaller value observed here must be due to the weak antiferromagnetic interactions between the paramagnetic centres.

KZ thanks the KRG-Scholarship program in "Human Capacity Development (HCDD)". EMP thanks the Panamanian agency SENACYT-IFARHU. J.S. thanks the Deutsche Forschungsgemeinschaft (SCHN/615-15) for continuous support. Supercomputing time at the LRZ Garching is gratefully acknowledged. REPW thanks the Royal Society for a Wolfson Merit Award.

## Notes and references

‡ Crystal data for 1  $[\text{C}_{159}\text{H}_{291}\text{Dy}_{10}\text{Co}_3\text{O}_{72}\text{P}_6\text{N}_3]$ :  $M_r = 5384.52$ , triclinic, space group  $P\bar{1}$ ,  $T = 150.1(8)$  K,  $a = 20.7198(8)$  Å,  $b = 23.4541(9)$  Å,  $c = 26.0799(15)$  Å,  $\alpha = 105.194(4)^\circ$ ,  $\beta = 93.035(4)^\circ$ ,  $\gamma = 103.129(3)^\circ$ ,  $V = 11825.6(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.512 \text{ g cm}^{-3}$ , total data = 65 089, independent reflections 41 489 ( $R_{\text{int}} = 0.0429$ ),  $\mu = 3.432 \text{ mm}^{-1}$ , 2169 parameters,  $R_1 = 0.0903$  for  $I \geq 2\sigma(I)$  and  $wR_2 = 0.2570$ . Unit cell parameters for 2  $[\text{C}_{159}\text{H}_{291}\text{Gd}_{10}\text{Co}_3\text{O}_{72}\text{P}_6\text{N}_3]$ : triclinic,  $a = 20.6870(4)$  Å,  $b = 23.3983(6)$  Å,  $c = 25.9194(7)$  Å,  $\alpha = 104.844(2)^\circ$ ,  $\beta = 93.166(18)^\circ$ ,  $\gamma = 103.3427(18)^\circ$ ,  $V = 11716.4(5)$  Å<sup>3</sup>. The data were recorded on an Agilent SuperNova CCD diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure of 1 was solved by direct methods and refined on  $F^2$  using SHELXTL.

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