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Centred nine-metal rings of lanthanides†

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Karzan H. Zangana,[a] Eufemio Moreno Pineda,[a] Eric J. L. McInnes,[a] Jürgen Schnack[b] and Richard E. P. Winpenny*[a]

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Two {Ln_{10}} 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[1] or metal cages.[2] In the second family there is a metal at the centre of the cage, and these are called either metallocrowns[3] or metallo-coronands.[4] Both classes have been studied, the former largely because of they can act as model compounds for studying physical phenomena, especially in magnetic molecules.[1] For metallocrowns studies extend to selective ion binding, as well as studies of interesting magnetic behaviour.[5] For both families most examples involve 3d-metal ions, although there are remarkable polymolybdate[2a] and palladium phosphonate rings.[2c] Several metal rings have been reported for the 4f-metals,[6] and for 3d–4f cages,[7] but many fewer centred cyclic structures.[8] Most rings and metallocrowns contain an even-number of metal sites in the cyclic portion, although metallocrowns are known with three[9] or five[10] metals in the backbone. Few large odd-numbered rings have been reported.[11] Here we report two cyclic {Ln_{10}} 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,[12] and we have reported a number of Co-4f cages.[13] We were intending to extend this work by reacting $[Ln_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ (Ln = Dy and Gd) with $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3](O_2C^tBu)$, $H_2O_3P^tBu$ and pyridine; the Co^{III} cage was used to try to control reactivity by using an inert 3d-metal and hence achieve a more predictable cage than using Co^{II} substrates.[13] 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 $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]$-$[Ln_{10}(O_2C^tBu)_{18}(O_3P^tBu)_6(OH)(H_2O)_4]$ (Ln = Dy **1**, Gd **2**) (Fig. 1).‡ The compounds are isostructural, and contain an anionic {Ln_{10}} cage co-crystallised with a $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]^+$ 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^{III} metal ions in a ring and a tenth Dy^{III} 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^{III} metal ions in the ring are arranged at the vertices of an approximately regular nonagon (or enneagon). The distances from the central

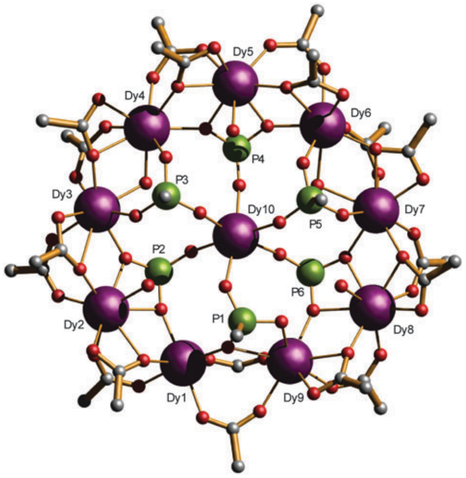

Fig. 1 Crystal structure of **1**. Colours: Dy, purple; P, green; O, red; C, grey. H-atoms and Me groups omitted for clarity.

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[a] School of Chemistry and Photon Science Institute, The University of Manchester, Oxford Road, Manchester M13 9PL, UK. E-mail: richard.winpenny@manchester.ac.uk; Fax: +44 (0)161-275-1001
[b] Department of Physics, The University of Bielefeld, Bielefeld, Germany

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Dy (Dy10) to the rim fall into two groups; there are longer contacts to Dy2, Dy5 and Dy8, averaging 5.92 ± 0.13 Å, while the remaining six contacts average 5.47 ± 0.12 Å. Eight of the distances between neighbouring Dy centres around the ring average 3.83 ± 0.13 Å; the ninth contact (Dy1···Dy9) is longer at 4.1496(2) Å.

Three of the six phosphonates lie below the plane of the $\{Dy_{10}\}$ disc (P2, P4, P6) and adopt the 4.221 binding mode (Harris notation[14]); 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 μ_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 μ-hydroxide (Dy–O distances of 2.308(12) and 2.294(11) Å) while the Dy6···Dy7 is bridged by a μ-water (Dy–O distances 2.537(12) and 2.635(12) Å).

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) Å, with *cis* O–Dy–O angles between 84.3(4) and 98.4(4)° while *trans* O–Dy–O angles like between 171.6(4) and 178.0(4)°. 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 $[Co_3(\mu_3\text{-}O)(O_2C^tBu)_6(py)_3]^+$ cationic triangle features Co^{III} sites around a central μ_3-oxide (Fig. S1, ESI†). Each cobalt is bound to five O-donors, from the central oxide and 2.11 bridging pivalates (av. Co–O distance = 1.89 Å), with a terminal pyridine (av. Co–N distance = 2.24 Å).

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 χ_M is the molar magnetic susceptibility) is 135.0 and 78.5 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^{III} sites (calc. $\chi_M T$ = 141.2 emu K mol^{-1} for ten Dy^{III} ions, $^6H_{15/2}$, $g = 4/3$; calc. $\chi_M T$ = 77.9 emu K mol^{-1} for ten Gd^{III} ions, $^8S_{7/2}$, $g = 1.99$). For **1** the $\chi_M T$ product gradually decreases until around 35 K and then decreases more rapidly. This behaviour is typical of Dy^{III} complexes and is due to depopulation of the Stark sub-levels.[15] **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 μ_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 μ_B, inset Fig. 2b). For **1**, the *M versus H/T* curve increases gradually with increasing field, reaching 52.2 μ_B at 7 T at 2 K without reaching saturation (Fig. S3, ESI†).

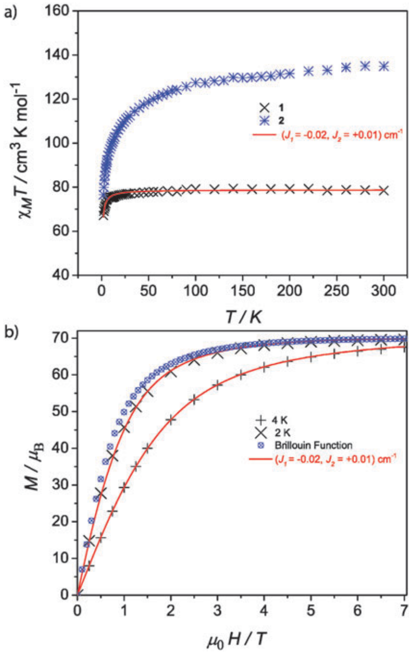

Fig. 2 (a) Variation of $\chi_M T$ with T for **1** and **2** in a magnetic field of 1000 Oe in the temperature range 2 to 300 K; (b) magnetisation against field for **2** from 0–7 T at 2 and 4 K, simulation and *Brillouin* function for 10 non-interacting Gd^{III} ions.

While it is presently impossible to model data for a $\{Dy_{10}\}$ cage, for the isotropic $\{Gd_{10}\}$ cage modern quasi approximate methods allow us to model the magnetic data, despite the 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.[16] 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:

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

where $\hat{\boldsymbol{s}}_i$ 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,† for further simulations). The best parameters are $J_1 = -0.02$, $J_2 = +0.01$ cm^{-1}. These numbers are barely distinguishable from zero, however they would generate a highly frustrated magnetic system, with the nine Gd^{III} 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[17] could only be seen at temperatures below 100 mK.

The large magnetisation value obtained for **2** and negligible anisotropy of Gd^{III} ($^8S_{7/2}$) makes this cluster a good candidate for MCE applications (Fig. S3, ESI†). The magnetic entropy changes of **2** for changing applied field can be calculated by the

Maxwell equation for magnetic entropy $(\partial S_m/dH)_T = (\partial M(T,M)/\partial T)H$ where the integration for an isothermal process yields $\Delta S = \int[\partial M(T,H)/\partial T]_H\,dH$.[18] This equation gives magnetic entropy change for **2** at 3 K and for a field changes ΔH = 0.5–7 T which corresponds to 28.5 J kg^{-1} K^{-1}. Much higher values have been reported for pure Gd-cages, for example 46.1 J kg^{-1} K^{-1} for a $\{Gd_{24}\}$ cage,[19] and for 3D Gd-frameworks, *e.g.* 59 J kg^{-1} K^{-1} for $[Gd(O_2CH)_3]_n$.[20] The smaller value observed here must be due to the weak antiferromagnetic interactions between the paramagnetic centres.

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Notes and references

‡ Crystal data for **1** $[C_{159}H_{291}Dy_{10}Co_3O_{72}P_6N_3]$: 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, α = 105.194(4)°, β = 93.035(4)°, γ = 103.129(3)°, V = 11825.6(10) Å^3, Z = 2, ρ = 1.512 g cm^{-3}, total data = 65 089, independent reflections 41 489 (R_{int} = 0.0429), μ = 3.432 mm^{-1}, 2169 parameters, R_1 = 0.0903 for $I \geq 2\sigma(I)$ and wR_2 = 0.2570. Unit cell parameters for **2** $[C_{159}H_{291}Gd_{10}Co_3O_{72}P_6N_3]$: triclinic, a = 20.6870(4) Å, b = 23.3983(6) Å, c = 25.9194(7) Å, α = 104.844(2)°, β = 93.166(18)°, γ = 103.3427(18)°, V = 11716.4(5) Å^3. The data were recorded on an Agilent SuperNova CCD diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) The structure of **1** was solved by direct methods and refined on F^2 using SHELXTL.

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