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## A bis-phenolate for the construction of linear lanthanide trimers§\*\*

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<sup>[§]</sup>Celebrating 300 years of Chemistry at The University of Edinburgh

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### Supporting information:

<sup>[†]</sup>Electronic supplementary information (ESI) available: Experimental detail, diagrams relating to magnetic studies (S1–S8), Crystallographic Information File (CIF) CCDC 945512 for 1 and unit cell parameters for 2 and 3. For ESI and crystallographic data in CIF or other electronic format see <http://dx.doi.org/10.1039/C3CC44996C>

## Abstract

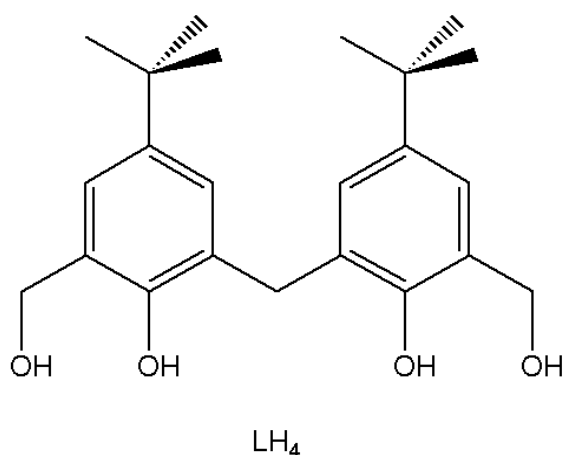
The ligand bis(5-tert-butyl-2-hydroxy-3-hydroxymethyl-phenyl)methane, a flexible calix[*n*]arene analogue, is employed to construct an unusual linear [Ln<sub>3</sub>] trimer.

## Main text

The chemistry of homo- and heteronuclear lanthanide clusters continues to attract intense academic interest. The stimulus for such varied research activity lies in the potential downstream applications of properties such as luminescence<sup>1</sup> and magnetism,<sup>2</sup> their use as building blocks in directed assembly,<sup>3</sup> and also in the aesthetically pleasing and diverse structures the clusters adopt. Examples of the latter include, supertetrahedral Ln<sub>20</sub> and Ln<sub>60</sub> species,<sup>4a,b</sup> a Gd<sub>36</sub>Ni<sub>12</sub> cluster<sup>4c</sup> and an icosidodecahedral Ni<sup>II</sup> cluster encapsulating a dodecahedron of La<sup>III</sup> ions.<sup>4d</sup> In terms of molecular magnetism the interest is two-fold. Magnetic refrigerants<sup>2c,d</sup> and Single-Molecule Magnets<sup>2e</sup> both require large-spin ground states, with the former requiring isotropy and the latter anisotropy in their ground state electronic configurations (among other desirable phenomena) and thus the rare-earth elements (particularly Gd, Tb and Dy) are logical candidates for constructing polymetallic clusters possessing interesting physical properties.

Our primary interests lie in the preparation, structural characterisation and magnetic analysis of polynuclear transition metal or lanthanide clusters. The metal core of such systems can vary in both shape and nuclearity, and moreover it is important to understand the effects that chemical structure has on the resulting magnetic exchange interactions, and ultimately the mechanisms by which they are influenced. Therefore the choice of cluster supporting ligand(s) is critical and a large exploration of ligand type (size, shape and donor ability) is crucial in ultimately gaining a degree of control of these (sometimes) complex and fascinating systems. Work in our group, and in others, has primarily focussed on using *p*-tert-butylcalix[*n*]arenes (TBC[*n*]s), predominantly TBC[4]<sup>5</sup> and TBC[8],<sup>6</sup> as ligands to support a range of 3d, 3d-4f and 4f polynuclear clusters. Calix[*n*]arenes are cyclic polyphenols that adopt well defined conformations as a consequence of the complementary hydrogen bonding interactions present at what is termed the lower-rim.<sup>7</sup> TBC[4] exists as a bowl-shaped molecule with an inherent cavity ideally suited to sequester a lanthanide (Ln, or a transition metal, TM) ion. This is exemplified with the isolation of a series of octahedral [Ln<sup>III</sup><sub>6</sub>(TBC[4])<sub>2</sub>] clusters (Ln = Gd, Tb, Dy).<sup>5g</sup> TBC[8] is a considerably more flexible ligand capable of adopting several conformers depending on the degree of phenolic deprotonation, as demonstrated via the synthesis of Ln<sub>x</sub> clusters (where x = 1-2 and 4-8).<sup>6b</sup> Polylanthanide cluster chemistry has also been explored with *p*-tert-butylldihomooxacalix[4]arene (TBHOC[4]), a ligand in which one methylene bridge has been replaced by an ethereal CH<sub>2</sub>OCH<sub>2</sub> bridge between two adjacent phenol moieties. In this case a series of isostructural Ln<sub>5</sub> clusters were isolated.<sup>8</sup> It is therefore clear that the nature of the polynuclear cluster isolated (and its corresponding magnetic properties) is strongly dependent on the supporting ligand. In this communication we

continue to examine the role of polyphenolic ligands, and have chosen bis(5-tert-butyl-2-hydroxy-3-hydroxymethylphenyl)methane,  $\text{LH}_4$ ,<sup>9</sup> as a candidate for polynuclear lanthanide cluster formation.  $\text{LH}_4$  is of particular interest because it bears a striking similarity to calix[ $n$ ]arenes, and can essentially be considered as half of a TBC[4]; it contains two *p*-tert-butylphenol moieties linked by a methylene bridge, and in addition contains methanol arms which resemble the ethereal linkages found in the oxacalixarenes (Figure 1). The four oxygen atoms of  $\text{LH}_4$  represents an attractive binding site to explore coordination chemistry, and it is somewhat surprising to discover that to date there is only one reported crystal structure where  $\text{LH}_4$  is coordinated to a metal of any type,<sup>10</sup> and no examples where  $\text{LH}_4$  is coordinated to a TM or Ln metal.

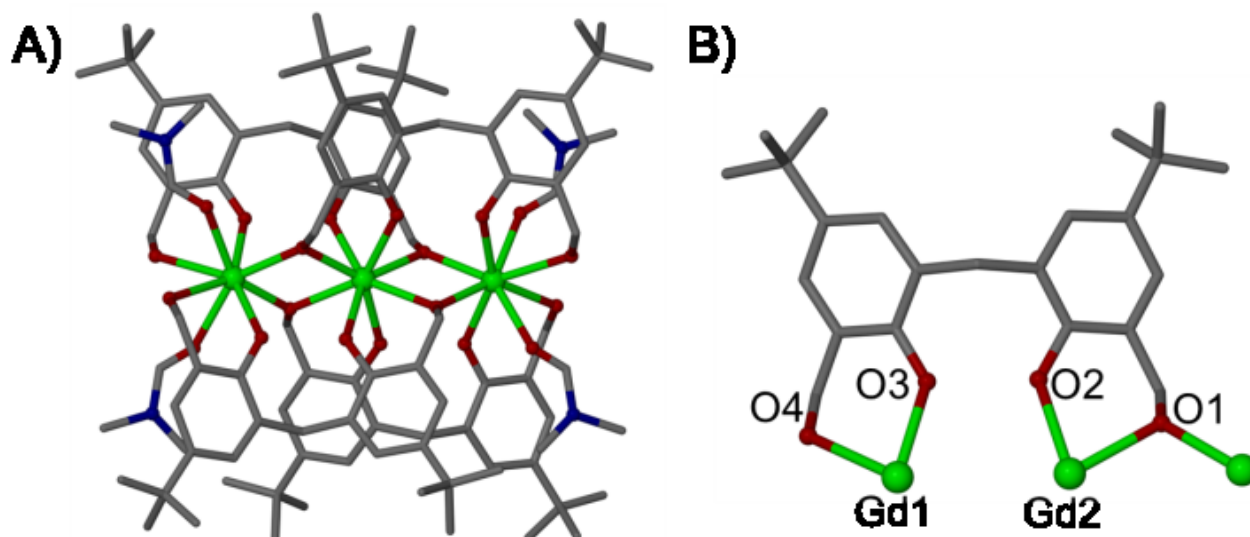


**Figure 1.** Structure of bis(5-tert-butyl-2-hydroxy-3-hydroxymethyl-phenyl)methane,  $\text{LH}_4$ .

The reaction of  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{LH}_4$  in a mixture of DMF/MeOH and in the presence of triethylamine, followed by vapour diffusion with acetonitrile, produced colourless crystals of **1–3** with general formula  $[\text{Ln}^{\text{III}}_3(\text{LH}_3)_4(\text{DMF})_4]$  (**1** = Gd; **2** = Tb; **3** = Dy; Figure 2). Crystals of **1** are in an orthorhombic cell and structure solution was performed in space group *Pnnn*. Compounds **1–3** are isostructural and thus a generic description of **1** is given here. The asymmetric unit in **1** contains a quarter of the molecule and symmetry expansion reveals that the metal core is a perfectly linear  $\text{Gd}^{\text{III}}$  trimer ( $\text{Gd1} \cdots \text{Gd2}$ , 3.723 Å;  $\text{Gd1-O1-Gd2}$ , 106.86°; Figure 2A) and is supported by four  $\text{LH}_{1.75}$  ligands.<sup>11</sup>

The  $\mu_3$ -bridging mode of the symmetry unique  $\text{LH}_{1.75}$  ligand is shown in Figure 2B. The peripheral alcoholic O-atoms are of two types: one (O1) bridges Gd1 and Gd2, while the other (O4) is terminally bound to Gd1 ( $\text{Gd1-O4}$ , 2.489(3) Å), while H-bonded to the co-crystallised solvent (*vide infra*). The phenolic O-atoms (O2, O3) are terminally bound to Gd2 and Gd1, respectively. Two DMF ligands (that are disordered over two positions) occupy coordination sites on each of the terminal  $\text{Gd}^{\text{III}}$  ions. Gd1 (and its symmetry equivalent, s.e.) has a distorted square antiprismatic geometry; its coordination sphere is occupied by the aforementioned DMF

ligands (O5–Gd1 2.438(3) Å), two phenolic oxygens (O–Gd1 2.393(2) Å) and two  $\eta$ -bridging methanolic oxygens (O–Gd1 2.271(2) Å). The central Gd2 is also distorted square antiprismatic, and its coordination sphere is occupied by four s.e.  $\eta$ -bridging methanolic oxygens (O1–Gd2 2.363(2) Å), and by four s.e. phenolic oxygen atoms (O2–Gd2 2.384(2) Å). Gd1 and Gd2 are thus housed within the two binding pockets present between the methanolic and phenolic oxygens of each LH<sub>1.75</sub>.



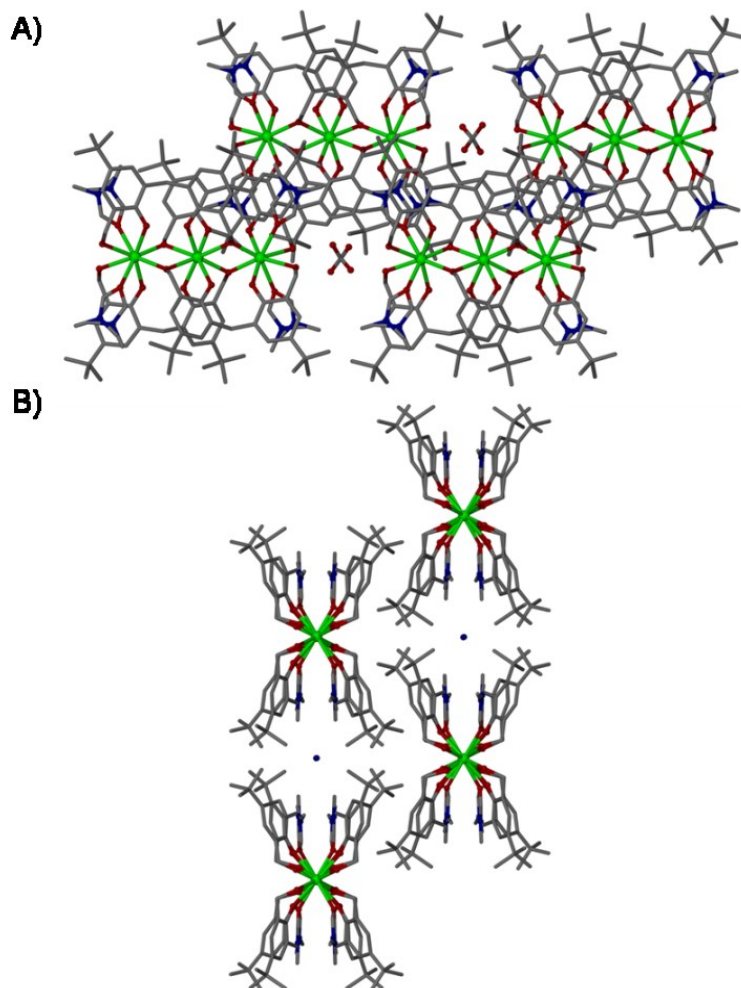
**Figure 2.** A) Symmetry expanded single crystal X-ray structure of **1**. B) Ligand coordination mode in **1**. Non-coordinating solvents and H atoms omitted for clarity. Colour code: C-grey; O-red; N-blue; Gd-green.

Further analysis of the extended structure reveals the presence of several co-crystallised solvent molecules (Figure 3). A methanol molecule is disordered over four positions and displays a s.e. close contact of 2.680 Å with the methanolic oxygen (O4) bonded to Gd1. This H-bonding interaction directs the assembly of molecules of **1** into linear chains along the direction coincident with the polynuclear Ln<sup>III</sup> axis (in the plane of the page in Figure 3A). Along one axis perpendicular to the Ln<sub>3</sub> chain, co-crystallised water and acetonitrile, both present at partial occupancy, reside in cavities generated by adjacent molecules of **1** (Figure 3B). A search of the CSD for Ln<sub>3</sub> complexes (Ln = Gd, Tb or Dy), where Ln is bonded to a phenolate reveal ca. 10 entries for Gd and Tb, about half of which conform to linear or near linear chains. For Dy there are ca. 20 entries, of which approximately half are Dy<sub>3</sub> chains. Complexes **1** – **3** are therefore rare examples of phenolate based Ln<sub>3</sub> chains. We believe that the combination of the ligand design (shape, binding mode and donor atoms) and the oxophilic nature of the lanthanides creates a predisposition of LH<sub>4</sub> and presumably related linear oligomers to construct Ln chains, although the latter will be the subject of future work.

The dc molar magnetic susceptibilities,  $\chi_M$ , of polycrystalline samples of **1-3** were measured over the 5 to 300

K temperature ( $T$ ) range in an applied magnetic field ( $H$ ) of 0.1 T. The experimental results for complex are plotted shown in Figure 4 in the form of the  $\chi_M T$  product, where  $\chi = M/H$  and  $M$  is the magnetisation of the sample. At 300 K the  $\chi_M T$  products of **1** ( $23.2 \text{ cm}^3 \text{ K mol}^{-1}$ ), **2** ( $35.5 \text{ cm}^3 \text{ K mol}^{-1}$ ) and **3** ( $42.2 \text{ cm}^3 \text{ K mol}^{-1}$ ) are close to that expected for three non-interacting  $\text{Gd}^{\text{III}}$  ( $S=7/2, L=0, J=7/2, g=2, {}^8\text{S}_{7/2}$ ),  $\text{Tb}^{\text{III}}$  ( $S=3, L=3, J=6, g=3/2, {}^7\text{F}_6$ ) and  $\text{Dy}^{\text{III}}$

( $S=5/2, L=5, J=15/2; g=4/3, {}^6\text{H}_{15/2}$ ) ions, respectively. On cooling in all three cases, the  $\chi_M T$  product remains essentially constant until approximately 100 K, below which the value begins to slowly decrease. For complexes **1** and **2**, this decrease continues to the lowest temperatures measured, indicative of the thermal depopulation of the single-ion ligand-field states and/or very weak antiferromagnetic exchange between the Ln centres.<sup>12</sup> For complex **3** a minimum of  $\sim 38.5 \text{ cm}^3 \text{ K mol}^{-1}$  at  $T = 20 \text{ K}$  is observed, before the  $\chi_M T$  product increases at lower temperatures to a maximum value of  $42.3 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K.

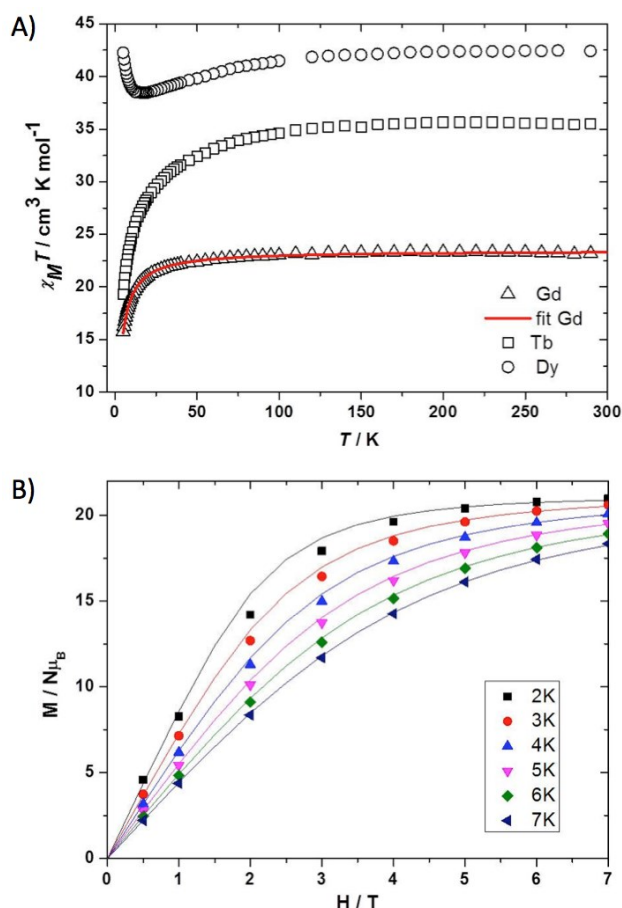


**Figure 3.** A) H- bonding with disordered and co-crystallised MeOH along the axis of the Ln<sup>III</sup> trimer. B) Perpendicular view of (A) showing disordered solvent occupying cavities between adjacent molecules of **1**.

This low temperature increase is suggestive of very weak ferromagnetic exchange between the constituent Dy<sup>III</sup> ions. We have used the isotropic spin-Hamiltonian (1) to model the magnetic properties of complex **1**:

$$\hat{H}_{iso} = -2 \sum_{i,j>i} J_{ij} \hat{S}_i \cdot \hat{S}_j + \mu_B H \sum_i g_i \hat{S}_i \quad (1)$$

where  $i$  and  $j$  are integers that index the constitutive single-ions in **1**,  $J$  is the isotropic exchange interaction parameter,  $\hat{S}$  is a spin operator,  $\mu_B$  is the Bohr magneton and  $g$  is the  $g$ -factor. For the numerical diagonalisation of the matrix representation of spin-Hamiltonian (1), we employed home written software (ITO-MAGFIT)<sup>13</sup> and spin-Hamiltonian (1) was fitted to the experimental data by use of the Levenberg–Marquardt algorithm.<sup>14</sup> For **1**, employing a model that assumes just one exchange interaction between nearest neighbours, this resulted in the best-fit parameter  $J_{Gd-Gd} = -0.07 \text{ cm}^{-1}$ , keeping the  $g$ -value fixed to 2. The magnetisation versus field data (Figure 4 and Figures S1-S2) for the same complex is satisfactorily fitted using the same parameter set. The so-obtained exchange interaction is comparable with previously reported alkoxide-bridged Gd<sup>III</sup> ions and is as expected for very weakly interacting  $4f$  ions.<sup>12</sup> In order to check for potential SMM behaviour in the Tb (**2**) and Dy (**3**) complexes, ac susceptibility studies were undertaken at temperatures below 10 K and in frequencies up to 1000 Hz. For complex **2** no out-of-phase behaviour was observed, but the tails of frequency dependent signals for **3** are observed below 6 K, indicative of the onset of slow magnetisation relaxation and SMM behaviour (Figure S3).



← **Figure 4.** A) Plot of the  $\chi_M T$  product versus  $T$  for complexes **1-3** in the 300 – 5 K temperature range, in an applied field of 0.1 T. Solid red line is a fit of the experimental data to Hamiltonian (1), see text for details. B) Plot of magnetisation ( $M/N\mu_B$ ) versus field ( $B$ ) for complex **1**. Solid lines are a fit of the experimental data to Hamiltonian (1), see text for details.

In summary  $\text{LH}_4$  has been shown to act as a ligand support for three isostructural polynuclear  $\text{Ln}_3$  chains ( $\text{Ln} = \text{Gd}, \text{Tb}$  and  $\text{Dy}$ ). The  $\text{Dy}$  analogue displays weak ferromagnetic exchange. Compounds **1** – **3** are the first examples of  $\text{LH}_4$  acting more generally as a ligand support for rare-earth clusters, and we believe that these compounds could presage a large number of new coordination complexes with  $3d$ , and  $3d-4f$  elements.

## Notes and references

‡ *Crystal data for 1*: C<sub>26.44</sub>H<sub>34.38</sub>Gd<sub>0.75</sub>N<sub>1.06</sub>O<sub>5.38</sub>,  $M = 570.99$ , Colourless Block,  $0.30 \times 0.28 \times 0.15 \text{ mm}^3$ , orthorhombic, space group *Pnnn* (No. 48),  $a = 15.9607(9)$ ,  $b = 17.0196(10)$ ,  $c = 19.2424(11) \text{ \AA}$ ,  $V = 5227.1(5) \text{ \AA}^3$ ,  $Z = 8$ , Bruker Apex II CCD diffractometer, Synchrotron radiation,  $\lambda = 0.77490 \text{ \AA}$ ,  $T = 100(2) \text{ K}$ ,  $2\theta_{\text{max}} = 67.2^\circ$ , 73454 reflections collected, 7930 unique ( $R_{\text{int}} = 0.0885$ ). Final  $\text{Goof} = 1.013$ ,  $RI = 0.0416$ ,  $wR2 = 0.1158$ ,  $R$  indices based on 5162 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ).

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