

## Lanthanide Complexes

# Decanuclear Ln<sub>10</sub> Wheels and Vertex-Shared Spirocyclic Ln<sub>5</sub> Cores: Synthesis, Structure, SMM Behavior, and MCE Properties\*\*

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**Abstract:** The reaction of a Schiff base ligand (LH<sub>3</sub>) with lanthanide salts, pivalic acid and triethylamine in 1:1:1:3 and 4:5:8:20 stoichiometric ratios results in the formation of decanuclear Ln<sub>10</sub> (Ln=Dy(1), Tb(2), and Gd (3)) and pentanuclear Ln<sub>5</sub> complexes (Ln=Gd (4), Tb (5), and Dy (6)), respectively. The formation of Ln<sub>10</sub> and Ln<sub>5</sub> complexes are fully governed by the stoichiometry of the reagents used. Detailed magnetic studies on these complexes (1–6) have been carried out. Complex 1 shows a SMM behavior with an effective

## Introduction

Polynuclear lanthanide complexes have caught the imagination of chemists and physicists in recent years for a variety of reasons.<sup>[1]</sup> Discovering new synthetic methods that allow the

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[**]	MCE = Magnetocaloric effect; SMM = Single-molecule magnet. Supporting information for this article (including molecular structures of 2– 5, details of the structural parameters for compounds 2–5 and magnetic data) is available on the WWW under http://dx.doi.org/10.1002/ chem.201501992.

energy barrier for the reversal of the magnetization ( $U_{eff}$ ) = 16.12(8) K and relaxation time ( $\tau_o$ )=3.3×10<sup>-5</sup> s under 4000 Oe direct current (dc) field. Complex **6** shows the frequency dependent maxima in the out-of-phase signal under zero dc field, without achieving maxima above 2 K. Complexes **3** and **4** show a large magnetocaloric effect with the following characteristic values:  $-\Delta S_m = 26.6 \text{ Jkg}^{-1} \text{ K}^{-1}$  at T = 2.2 K for **3** and  $-\Delta S_m = 27.1 \text{ Jkg}^{-1} \text{ K}^{-1}$  at T = 2.4 K for **4**, both for an applied field change of 7 T.

modulation of the nuclearity and topology of such complexes is an endeavor that is being pursued vigorously by chemists, whereas the magnetic properties of such complexes (singlemolecule magnetism<sup>[2]</sup> and magnetocaloric effect<sup>[3]</sup>) are of interest to chemists and physicists alike. In this context, polynuclear lanthanide complexes where the nuclearity is 5 or 10 are quite sparse. Our interest in such systems has emanated from our recent forays in this field in which we have been able, by utilizing hydrazone Schiff base ligands, to assemble tetra-,<sup>[4a,b]</sup> hexa-<sup>[4c]</sup> and octanuclear<sup>[4d]</sup> complexes. The latter possessed a new cyclooctadiene-type of conformation.[4d] We were interested to extend the nuclearity of the macrocycle through a judicious choice of a suitable multidentate ligand. Caneschi, et al. has previously reported a Dy<sub>10</sub> macrocycle using methoxy ethanol as the ligand but only measured its static magnetism.<sup>[5a]</sup> Since then, other examples, though sparse, are becoming known. Similar to decanuclear complexes,<sup>[5]</sup> pentanuclear<sup>[6]</sup> analogues are equally rare; in fact, only four previous families are known. It is worth noting that some cyclic Dy<sub>3</sub>,<sup>[7]</sup> Dy<sub>4</sub>,<sup>[8]</sup> and Dy<sub>6</sub><sup>[9]</sup> complexes have been shown to exhibit a toroidal magnetic moment in the ground state, which is due to the noncollinear arrangement of the local magnetic moments of the individual Dy<sup>III</sup> centers. Moreover, most of these systems present SMM behavior, which is associated with the thermally excited spin states of the Dyn molecule. These systems, also called single-molecule toroics (SMTs), are promising candidates for future applications in quantum computing and information storage. It should be mentioned that the linkage of two and even more cyclic Dy<sub>3</sub> SMTs give rise to coupled systems in which the toroidal ground sate is robust because the easy axial anisotropy axes are very difficult to modify by the interaction between the coupled units.<sup>[9,10]</sup>

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Chem. Eur. J. 2015, 21, 16955 - 16967



Herein, we report a new chelating, flexible, and sterically unencumbered multisite coordinating ligand (E)-2-((2-hydroxyethylimino)methyl)-6-(hydroxymethyl)-4-methylphenol  $(LH_3),$ which allows the assembly of both deca- and pentanuclear lanthanide complexes. Most interestingly, both these new families of polynuclear lanthanide complexes do not contain oxide/hydroxide ligands, which are commonly found in many such complexes. Accordingly, herein, we report the synthesis, structural characterization, and magnetic studies of  $[Ln_{10}(LH)_{10}(\kappa^2 Piv_{10}$  · XCHCl<sub>3</sub>·YCH<sub>3</sub>CN·PH<sub>2</sub>O·Q MeOH (1, Ln = Dy<sup>III</sup>, X = 9, Y = 4; **2**, Ln=Tb<sup>III</sup>, X=8, Y=4; **3**, Ln=Gd<sup>III</sup>, X=8, Y=3, P=5;) and  $[Ln_5(LH)_4(\mu_2-\eta^1\eta^1Piv)_4(\eta^1Piv)(S)]$ ·XH<sub>2</sub>O·YCH<sub>3</sub>OH (4, Ln = Gd<sup>III</sup>, S = MeOH, X=3, Y=1; **5**, Ln=Tb<sup>III</sup>, S=H<sub>2</sub>O, X=3, Y=2; **6**, Ln=  $Dy^{III}$ , S=MeOH, X=2, Y=1). Whereas 1-3 are metallamacrocycles, compounds 4-6 possess a pentanuclear core constructed by two Ln<sub>3</sub> triangles sharing a common lanthanide ion.

## **Results and Discussion**

## Synthesis

Recently, we have been experimenting with various types of ligands for the purpose of knowing their discriminatory capability in terms of directing homonuclear lanthanide assemblies versus heteronuclear 3d/4f complexes.<sup>[11]</sup> Thus, the ligands, 2-(hydroxymethyl)-6-carbaldehyde-4-methylphenol (**C2**) and the Schiff base derivative (2-(2-hydroxy-3-(hydroxymethyl)-5-methylbenzylideneamino)-2-methylpropane1,3-diol) afforded pentanuclear  $M_4Ln^{[11a,b]}$  and  $M_2Ln^{[11c,d,e]}$  derivatives respectively (Scheme 1).

Neither of these ligands, however, was able to assemble homonuclear lanthanide complexes. We reasoned that whereas **C2** does not possess enough flexible coordinating pockets, its Schiff base derivative 2-(2-hydroxy-3-(hydroxymethyl)-5-methylbenzylideneamino)-2-methylpropane1,3-diol (Scheme 1b) has two  $-CH_2OH$  arms fused to the same carbon center making it a rigid system. Such rigid ligands are generally not suitable for polynuclear lanthanide complex assembly. To overcome these drawbacks we have designed a new chelating, flexible, and sterically unencumbered multisite coordinating compartmental Schiff base ligand (*E*)-2-((2-hydroxyethylimino)methyl)-6-(hydroxymethyl)-4-methylphenol (LH<sub>3</sub>). The ligand LH<sub>3</sub> was prepared by a two-step synthetic protocol involving the conversion of the precursor **C1** to **C2** and its subsequent condensation with 2-amino ethanol (Scheme 2).

LH<sub>3</sub> contains two coordination compartments; one of these possesses a phenolic oxygen and a benzyl oxygen atom (chelating OO donor). The other compartment consists of a phenolic oxygen and a flexible ethanolamine group (tridentate ONO donor) (Scheme 3).

Thus, potentially  $LH_3$  contains four divergent coordinating centers all of which are anticipated to participate in coordination to construct a homometallic ensemble. Also, we are aware that the  $-CH_2OH$  unit can bind both in its native and deprotonated forms. In the latter it can act as a bridging ligand and enable formation of larger polynuclear complexes. In this synthesis we also utilized pivalic acid as a co-ligand because of



Scheme 1. a) Pentanuclear  $M_4Ln^{(11a,b)}$  and b) trinuclear  $M_2Ln^{(11c,d,e)}$  derived from C2 and its Schiff base derivative, respectively.



Scheme 2. Synthesis of LH<sub>3</sub>.

the propensity of the pivalate ion to bridge adjacent metal centers.<sup>[12,4b,d]</sup> Treatment of  $LH_3$  with  $Ln^{III}$  salts along with pivalic acid in the presence of triethylamine under two different conditions afforded deca- (1–3) and pentanuclear complexes (4–6) (Scheme 4).

A subtle variation in stoichiometry, including that of the base triethylamine, causes an interesting deprotonation behav-

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Chem.	EUI. J.	2015,	21,	10933 -	10907





Scheme 3. The two distinct coordination compartments of LH<sub>3</sub>. Site 1 contains a chelating OO coordination manifold whereas Site 2 provides ONO cavity.

ior. Thus, in the decanuclear complexes, **1–3**, the =N–CH<sub>2</sub>CH<sub>2</sub>OH is deprotonated whereas the – CH<sub>2</sub>OH arm is not. In the case of the pentanuclear complexes the situation is reversed. The molecular structures of **1–6** were delineated by their single-crystal diffraction studies as outlined below.

#### X-ray crystal structures of 1-3

Single-crystal X-ray analysis reveals that 1-3 crystallize in the triclinic system in the centrosymmetric P1 space group with Z=2. The asym-

LnCl<sub>3</sub> · 6H<sub>2</sub>O

metric unit of 1–3 consists of two half molecules, that is,  $[Ln_s(LH)_s(Piv)_s]$  in which Ln = Dy (1), Tb (2), and Gd (3). Because of the structural similarity of 1–3, only the structure of 1 is described, here, in detail. The others are given in the Supporting Information.

The molecular structure of **1** is given in Figure 1; those of **2** and **3** are given in the Supporting Information (Figures S1 and S2). Selected bond parameters of **1** are summarized in the Table 1. Other bond parameters including those of **2** and **3** are given in the Supporting Information (the Supporting Information, Tables S1 and S2).



**Figure 1.** a) Molecular structure of 1 (hydrogen atoms and the solvent molecules have been omitted for clarity). b) The  $Dy_{10}$  metallacycle possessing a chair–chair–chair conformation.

The crystal structure of **1** (Figure 1 a) reveals it to be a macrocycle that is assembled as a result of the cumulative coordination action of ten  $[LH]^{2-}$  ligands, each of which binds in a  $\mu_3$ - $\eta^2$ : $\eta^1$ : $\eta^2$ : $\eta^1$  fashion (Scheme 5). In addition to  $[LH]^{2-}$ , ten pivalate ions participate in coordination, each of which being involved in binding to only one Dy<sup>III</sup> ion. Most interestingly,



Scheme 5. Binding mode of the ligand  $[LH]^{2-}$  with  $Dy^{III}$  ions.

compound **1** does not contain any other common ligands such as oxide or hydroxide, which are generally found in polynuclear lanthanide complexes.

An analysis of the molecular structure of **1** reveals that the macrocycle contains interconnected  $Dy_2O_2$  four-membered rings possessing spirocyclic  $Dy^{III}$  nodes. The macrocycle itself is 20-membered, considering the shortest Dy-O-Dy pathway. The  $Dy^{III}$  ions organize themselves in the complex in a chair-chair-chair conformation (Figure 1b).

The assembly of the macrocycle 1 is accomplished in the following manner. The four-membered non-planar Dy<sub>2</sub>O<sub>2</sub> ring is built by the coordination action of bridging phenolate and =NCH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup> that emanate from two different ligands. The inter-Dy<sup>III</sup> distances and the Dy–O–Dy angles in the four-membered rings are in the range 3.797-3.831 Å and 105.60 (2)-114.85(1)° respectively. All the Dy<sup>III</sup> centers are eight-coordinate



Ln = Tb, X = 8, Y = 4 (2) Ln = Gd, X = 8, Y = 3, P = 5 (3)

CHC

 $P H_2 O$ Ln = Dy. X = 9. Y = 4 (1)

CH3CM

Chem. Eur. J. 2015, 21, 16955 - 16967

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X H<sub>2</sub>O

Y CH<sub>3</sub>OH

 $Ln = Gd, S = MeOH, X = 3, Y = 1 (4) \\ Ln = Tb, S = H_2O, X = 3, Y = 0 (5) \\ Ln = Dy, S = MeOH, X = 2, Y = 1 (6)$ 



Table 1. Selected bond length [Å] and bond angle [°] parameters for 1. <sup>[a]</sup>					
Dy(1P)-O(13P) <sup>[a]</sup> Dy(1P)-O(1P) Dy(1P)-O(2P) Dy(1P)-O(6P) Dy(1P)-O(5P) Dy(1P)-O(17P) Dy(1P)-O(16P) Dy(1P)-O(16P)	2.237(4) 2.294(4) 2.386(4) 2.402(4) 2.438(4) 2.454(4) 2.459(4) 2.459(4)	Dy(2P)-O(18P) Dy(3P)-O(4P) Dy(3P)-O(7P) Dy(3P)-O(8P) Dy(3P)-O(12P) Dy(3P)-O(11P) Dy(3P)-N(3P) Dy(3P)-N(3P)	2.474(4) 2.237(4) 2.300(4) 2.363(4) 2.395(4) 2.431(4) 2.447(5) 2.447(5)	Dy(5P)-O(14P) Dy(5P)-O(14P) Dy(5P)-O(3P) Dy(5P)-O(2P)* Dy(5P)-N(5P) Dy(5P)-O(24P) Dy(5P)-O(25P) Dy(5P)-O(25P)	2.376(4) 2.376(4) 2.414(4) 2.420(4) 2.455(5) 2.462(4) 2.467(4) 2.840(6)
Dy(1P)-N(1P) Dy(1P)-Dy(5P) <sup>[a]</sup> Dy(2P)-O(1P) Dy(2P)-O(4P) Dy(2P)-O(5P) Dy(2P)-O(9P) Dy(2P)-O(8P) Dy(2P)-O(19P) Dy(2P)-N(2P)	2.460(5) 3.8107(4) 2.247(4) 2.303(4) 2.356(4) 2.397(4) 2.424(4) 2.438(5) 2.468(5)	Dy(3P)-O(21P) Dy(3P)-O(20P) Dy(4P)-O(7P) Dy(4P)-O(10P) Dy(4P)-O(11P) Dy(4P)-O(15P) Dy(4P)-O(14P) Dy(4P)-O(23P) Dy(4P)-N(4P) Dy(4P)-O(22P)	2.402(4) 2.498(4) 2.232(4) 2.303(4) 2.371(4) 2.380(4) 2.418(4) 2.447(4) 2.464(5) 2.508(4)	Dy(4P)((71P) Dy(5P)-O(10P) Dy(5P)-O(13P) Dy(2P)-O(1P)-Dy(1P) Dy(1P)-O(2P)-Dy(5P)* Dy(3P)-O(4P)-Dy(2P) Dy(2P)-O(5P)-Dy(1P) Dy(4P)-O(7P)-Dy(3P) Dy(3P)-O(8P)-Dy(2P) Dy(5P)-O(10P)-Dy(4P) Dy(5P)-O(10P)-Dy(4P)	2.849(0) 2.242(4) 2.304(4) 114.61(17 104.91(15 113.53(16 105.70(15 114.85(19) 104.97(14 114.63(16
[a] Symmetry trans	formations used	l to generate equiva	lent atoms: 1–	Dy(4P)-O(11P)-Dy(3P) Dy(1P)*-O(13P)-Dy(5P) Dy(5P)-O(14P)-Dy(4P) x+1, -y+1, -z+1.	105.33(15 114.10(16 105.85(14



**Figure 2.** a) Twenty-membered macrocyclic core. b) A distorted-triangular dodecahedral geometry around the Dy<sup>III</sup> ion.

(7O, 1N) and possess a distorted-triangular dodecahedral geometry (Figure 2 b).

A few further comments on the molecular structure of 1. With respect to the mean plane (considering all the Dy atoms) of the macrocycle, alternate Dy atoms lie above and below (average 0.578 (7) Å) the plane (Figure 2a). Interestingly, each LH<sup>2-</sup> alternately is placed above and below the plane of the Dy<sub>10</sub> wheel. Complex 1 displays strong intramolecular O-H···O (2.187 (6) Å) hydrogen-bonding interactions between the pivalic carboxylate oxygen atoms and the Dy-coordinated benzyl alcohol (--CH<sub>2</sub>OH) arms (Figure 1 a). The supramolecular structure of 1 reveals a 2D architecture, in which a chloroform channel is found where the trapped chloroform molecules are stabilized by hydrogen-bonding interactions (Supporting Information, Figures S3 and S4). An idea about the macrocyclic ring size of 1 can be obtained from the distances between the symmetry equivalent Dy atoms, which are in the range 11.696 (6) to 11.976 (7) Å.

In spite of the large interest in 4f complexes, surprisingly, only a few  $Ln_{10}$  complexes are known in literature. As mentioned earlier, in 2003 Caneschi and co-workers first reported a  $Dy_{10}$  wheel containing methoxyethanol as a bridging ligand.<sup>[5a]</sup> The molecular topology of **1** is similar to this literature precedent although the ligands used are entirely different. An-

other example of decanuclear complexes {Ln<sub>10</sub>} (Ln = Dy or Gd) reveals that nine Dy<sup>III</sup> metal ions are present in a ring whereas a tenth Dy<sup>III</sup> metal ion is located at the center of the structure.<sup>[5b]</sup> Finally, another Dy<sub>10</sub> ensemble is known containing vertex-fused Dy<sub>3</sub> triangles<sup>[5c]</sup> (Figure 3).

## X-ray crystal structures of 4-6

X-ray crystallographic analysis of **4–6** reveals that all these complexes crystallize in the monoclinic system in the  $P2_1$  chiral space group with Z=2. Compounds **4–6** are neutral and possess a nearly similar structural arrangement with only minor





Figure 3. Examples of reported discrete decanuclear lanthanide complexes.

structural variations (Scheme 4 and Supporting Information). The asymmetric unit of **4–6** consists of a full molecule  $[Ln_5(LH)_4(\mu_2-\eta^1\eta^1\text{Piv})_4(\eta^1\text{Piv})(\text{MeOH}/\text{H}_2\text{O})]$ . The refined Flack parameters of **4–6** are 0.010(13), -0.003(10), and 0.013(11), respectively, indicating the crystallization of enantiopure forms.

In view of their structural similarity, we describe, herein, the molecular structure of 6 as a representative example; the structural details of 4 and 5 are given in the Supporting Information (Figures S5 and S6). A perspective view of the molecular structure of 6 is depicted in Figure 4. The caption of Fig-

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Figure 4. Molecular structure of 6 (hydrogen atoms and the solvent molecules have been omitted for clarity). Selected bond lengths [Å] and bond angle [°] parameters are as follows: Dy(1)-O(2) = 2.343(7); Dy(1)-O(6) = 2.382(7); Dy(1)-O(9) = 2.396(7); Dy(1)-N(1) = 2.452(10); Dy(1)-O(1) = 2.516(8); Dy(2)-O(5) = 2.317(6); Dy(2)-O(12) = 2.404(6); Dy(2)-N(2) = 2.433(8); Dy(2)-O(3) = 2.460(7); Dy(2)-O(4) = 2.513(8); Dy(3)-O(8) = 2.367(6); Dy(3)-O(3) = 2.425(6); Dy(3)-N(3) = 2.437(8); Dy(3)-O(12) = 2.456(6); Dy(3)-O(7) = 2.535(7); Dy(4)-O(11) = 2.327(7); Dy(4)-O(6) = 2.445(7); Dy(4)-N(4) = 2.451(9); Dy(4)-O(9) = 2.460(7); Dy(4)-O(10) = 2.474(8); Dy(5)-O(3) = 2.300(6); Dy(5)-O(9) = 2.302(7); Dy(5)-O(12) = 2.313(6); Dy(5)-O(6) = 2.330(6); Dy(5)-O(5) = 2.366(6); Dy(5)-O(11) = 2.368(6); Dy(5)-O(8) = 2.377(6); Dy(5)-O(2) = 2.399(7); Dy(5)-O(3)-Dy(3) = 97.06(2); Dy(3)-O(3)-Dy(2) = 97.07(2); Dy(5)-O(3)-Dy(2) = 96.16(2); Dy(2)-O(5)-Dy(5) = 98.33(2); Dy(5)-O(6)-Dy(1) = 97.41(2); Dy(5)-O(6)-Dy(4) = 95.79(2); Dy(1)-O(6)-Dy(4) = 98.17(3); Dy(3)-O(8)-Dy(5) = 96.53(2); Dy(5)-O(9)-Dy(1) = 97.74(3); Dy(5)-O(9)-Dy(4) = 96.10(3); Dy(1)-O(9)-Dy(4) = 97.32(2); Dy(4)-O(11)-Dy(5) = 98.02(2); Dy(5)-O(12)-Dy(2) = 97.28(2); Dy(5)-O(12)-Dy(3) = 95.74(2); Dy(2)-O(12)-Dy(3) = 97.66(2).

ures 4 and 5 a summarizes the selected bond parameters of **6**. The molecular structures and selected bond parameters of the other two compounds (**4** and **5**) are given in the Supporting Information (Figure S5 and S6, Tables S3–S4).

The molecular structure of **6** reveals that the five Dy<sup>III</sup> ions are held together by four doubly deprotonated  $[LH]^{2-}$  heptadentate Schiff base ligands. Each such ligand holds four different Dy<sup>III</sup> ions in a  $\mu_4$ - $\eta^3$ : $\eta^2$ : $\eta^1$ : $\eta^1$  fashion (Scheme 6).

Each ligand provides one benzyl alcoholic  $\mu_3$ -oxygen atom, one phenolic  $\mu_2$ -oxygen, and one unidentate flexible chelating ethanolamine group (bidentate NO donor) (Scheme 6). Further



**Scheme 6.** Binding mode of the ligand [LH]<sup>2-</sup> with Dy<sup>III</sup> ions.

tate NO donor) (Scheme 6). Further analysis of the structure of **6** reveals some interesting features. Compound **6** contains a pentanuclear  $[Dy_5(\mu_3-O)_4(\mu_2-O)_4]^{+7}$  core consisting of triangular motifs  $[Dy_3(\mu_3-O)_2(\mu_2-O)_2]^{+5}$  that are fused with each other through a common vertex (Dy5) (Figure 5). Each triangular unit is capped by two  $\mu_3$ -O deprotonated benzyl alcohol oxygen atoms derived from two



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Figure 5. a) Vertex-fused triangular unit capped by two  $\mu_3$ -O alkoxy group from above or below face of the triangle. Intermetallic distances [Å] and angles [°]: Dy2-Dy3 = 3.658(12); Dy2-Dy5 = 3.541(9); Dy3-Dy5 = 3.540(12); Dy5-Dy4 = 3.542(9); Dy1-Dy4 = 3.648(8); Dy5-Dy1 = 3.539(13); Dy2-Dy3-Dy5 = 58.91(1); Dy5-Dy2-Dy3 = 62.21(2); Dy3-Dy2-Dy5 = 58.87(1); Dy5-Dy4-Dy1 = 58.94(1); Dy5-Dy1 = 60.02(2); Dy5-Dy1-Dy4 = 59.09(2); b) Nonplanar disposition of the vertex fused triangular unit.

separate ligands. The  $\mu_2$ -O phenolate oxygen atoms bridge the edges of the triangles. In addition to the binding provided by LH<sup>2-</sup>, the peripheral Dy<sup>III</sup> ions are further held together as a result of two  $\mu_2$ - $\eta^1$ : $\eta^1$  binding action of the pivalate anions. Finally, to satisfy the charge and coordination requirements, other pivalate anions coordinate the terminal Dy<sup>III</sup> ions in a monodentate fashion.

As mentioned above, the pentanuclear  $Dy_5$  core consists of two interconnected  $Dy_3$  motifs. The dihedral angle between these two is 60.78(2)<sup>°</sup>. In addition, the central dysprosium ion (Dy5) is part of six  $Dy_2O_2$  four-membered rings (Figure 5 b).

Finally, the central  $Dy^{III}$  in **6** is eight-coordinated in an alloxygen coordination environment and in a distorted-triangular dodecahedral geometry (Figure 6a). In contrast, the peripheral  $Dy^{III}$  ions, although also eight-coordinate, possess a different coordination environment (70,1N) and geometry (distorted square antiprism geometry) (Figure 6b).

Interestingly, again, it is surprising to note that only a handful of Ln<sub>5</sub> complexes<sup>[6]</sup> whose magnetic behavior has been well-studied are known in the literature. Some of these are summarized in Figure 7, revealing that three structural types are thus far known, that is, square-pyramidal,<sup>[6a-c]</sup> trigonal bipyramidal<sup>[6d]</sup> and butterfly-shaped.<sup>[6e]</sup> The current family, thus represents a new structural type among pentanuclear Ln<sub>5</sub> complexes. Again, similar to the decanuclear complexes, the pentanuclear complexes reported herein do not contain  $O^{2-}/OH^{-}$  ligands.



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Figure 6. Different geometries around octa-coordinated Dy<sup>III</sup> ions: a) Distorted-triangular dodecahedral and b) distorted square-antiprism geometry.



**Figure 7.** Examples of reported discrete pentanuclear lanthanide complexes<sup>(6)</sup> having a) square pyramidal, b) trigonal bipyramidal, and c) butterfly core.

## **Magnetothermal properties**

The temperature dependence of  $\chi_M T$  for complexes **1–6** ( $\chi_M$  is the molar magnetic susceptibility per Ln<sub>n</sub> unit) in the range



Figure 8. Temperature dependence of the  $\chi_M T$  product for complexes 1–6. The black solid lines show the best fits for complexes 3 and 4.

300–2 K were measured in an applied magnetic field of 0.1 T (Figure 8).

The room temperature  $\chi_M T$  values for complexes **1–6** are close to those calculated for isolated Ln<sup>III</sup> ions in the free-ion approximation (Table 2).

We start with the simpler cases concerning the Gd complexes **3** and **4**. On cooling, the  $\chi_M T$  product for **3** and **4** remains almost constant until  $\approx 75$  and 100 K, respectively, and then it decreases sharply down to 2 K. Because Gd<sup>3+</sup> ions present no first order spin–orbit coupling, the decrease of the  $\chi_M T$ product at low temperature is mainly due to the presence of a very weak antiferromagnetic interaction between the Gd<sup>3+</sup> ions and/or zero-field splitting (ZFS) effects of the ground state. This is supported by the field dependence of the magnetization at 2 K for **3** and **4**, which are well below the Brillouin function for ten and five non-interacting Gd<sup>3+</sup> ions, respectively (Figure 9). At high field the saturation of the magnetization



**Figure 9.** Field dependence of the magnetization for complexes 1-6 at 2 K. The black solid lines represent the Brillouin function for non-interacting  $Gd^{3+}$  ions.

is almost complete at 5 T, reaching values that agree well with the theoretical saturation values for ten and five  $Gd^{3+}$  ions, respectively.

The magnitude of the antiferromagnetic exchange interaction in **3** could not be determined by diagonalization matrix methods because of the extremely high dimension of the matrices to be diagonalized for a  $Gd_{10}$  system. Nevertheless, to estimate the value of the magnetic exchange coupling mediated by the  $\mu$ -alkoxido/ $\mu$ -phenoxido pathway in **3** we have used a very crude model, in which each wheel has been considered to be formed by ten mononuclear Gd units and the intermononuclear interactions calculated by using the molecular field

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16960



Compound	Spin-orbit ground state of the Ln <sup>3+</sup> ion	$\chi_M T$ theoretical <sup>[a]</sup> /at 300 K/ at 2 K [cm <sup>3</sup> Kmol <sup>-1</sup> ]	Calculated saturation value <sup>[b]</sup> , <i>M</i> at 2 K and 5 T [N $\mu_B$ ]
1	${}^{6}H_{15/2}, g_{J} = 4/3$	141.7/141.30/99.19	100/55.54
6	${}^{6}H_{15/2}, g_{\rm J}=4/3$	70.85/74.17/34.99	50/30.59
3	${}^{8}S_{7/2}$ , $g_{1}=2$	78.75/82.12/41.56	35/34.40
4	${}^{8}S_{7/2}, g_{J} = 2$	39.375/40.77/22.67	70.0/70.64
2	$^{7}F_{6}, g_{J} = 3/2$	118.2/123.80/64.64	90/50.12
5	$^{7}F_{6}, q_{1} = 3/2$	59.10/64.65/17.09	45/27.43

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dialkoxo and diphenoxo-bridged  $Gd^{3+}$  complexes, with or without carboxylate bridges connecting the  $Gd^{3+}$  ions.<sup>[13]</sup> The structural differences between the  $Gd_2O_2$  bridging fragments involving short and long Gd--Gd distances could be responsible for the different magnetic coupling of the two magnetic pathways. In this regard, theoretical and experimental studies carried out on oxygen-bridged  $Gd_2$  complexes

theory. Taking into account the above considerations, the experimental data were analyzed with the following Hamiltonian:

$$\hat{H} = zJ' < S_z > \hat{S}_z + g_i\beta H \sum_i \hat{S}_i$$

The best fitting parameters were  $zJ' = -0.0127(1) \text{ cm}^{-1}$  and g = 2.054(1). Although the obtained values are similar to the reported coupling constants for dialkoxo- and diphenoxobridged Gd<sup>3+</sup> complexes, with or without carboxylate bridges connecting the Gd<sup>3+</sup> ions,<sup>[13]</sup> they should be taken with caution because of 1) the crudeness of the model and 2) the possible existence of ZFS splitting of the Gd<sup>3+</sup> ions.

As indicated above, compound **4** exhibits a structure that consists of two vertex fused triangles with two different types of bridging units between the Gd<sup>3+</sup> ions: i) Di- $\mu_3$ -dialkoxido/ $\mu$ -phenoxido, linking the central Gd<sup>3+</sup> ion to the outer counterparts with Gd–Gd distances of approximately 3.540 Å, and ii) di- $\mu_3$ -dialkoxido/di- $\mu$ -syn-syn pivalato connecting each couple of outer Gd<sup>3+</sup> ions with Gd–Gd distances of approximately 3.650 Å. Although the Gd–Gd distances slightly differ between the two fused triangles, to analyze the magnetic properties the four Gd–Gd distances corresponding to the type (i) bridging fragments were considered to be all equal. Likewise, the two outer type (ii) distances were considered to be equal. Taking into account the above considerations, the magnetic properties of **4** were modeled using the following two-*J* isotropic Hamiltonian:

$$\begin{split} \hat{H} &= -J_1(\hat{S}_{Gd1}\hat{S}_{Gd5} + \hat{S}_{Gd2}\hat{S}_{Gd5} + \hat{S}_{Gd3}\hat{S}_{Gd5} + \hat{S}_{Gd4}\hat{S}_{Gd5}) - \\ J_2(\hat{S}_{Gd1}\hat{S}_{Gd4} + \hat{S}_{Gd2}\hat{S}_{Gd3}) \end{split}$$

in which  $J_1$  and  $J_2$  describe the magnetic exchange pathways involving short and long Gd···Gd distances, respectively (Figures 5 and 10).

The  $D_{\rm Gd}$  is assumed negligible, because this ion is rather isotropic. The simultaneous fit of the experimental magnetization and susceptibility data with the above Hamiltonian using the PHI program<sup>[14]</sup> afforded the following set of parameters:  $J_1 = -0.15 \text{ cm}^{-1}$ ,  $J_2 = -0.072 \text{ cm}^{-1}$  and g = 2.04 with  $R = 5 \times 10^{-5}$   $(R = \Sigma(\chi_{\rm obs}T \chi_{\rm calc}T)^2/\Sigma(\chi_{\rm obs}T)^2)$ , in which  $\chi_{\rm calc}$  and  $\chi_{\rm obs}$  denote calculated and observed molar magnetic susceptibilities, respectively. As in the case of compound **3**, the obtained values are in good agreement with the reported coupling constants for



Figure 10. Coupling scheme for complex 4.

(alkoxido, phenoxido, and carboxylate) complexes have suggested that *J* becomes more negative as the Gd–O–Gd, and consequently the Gd····Gd, decrease.<sup>[13a,f]</sup> The extracted *J* values for **3** and **4** agree well with this hypothesis as the former, which has larger Gd–O–Gd angles and Gd–Gd distances, exhibits the weaker Gd–Gd magnetic exchange interactions. In **4**, the shorter di- $\mu_3$ -dialkoxido/ $\mu$ -phenoxido magnetic exchange pathway, linking the central and outer Gd<sup>3+</sup> ions exhibits the stronger magnetic exchange coupling, whereas the long di- $\mu_3$ -dialkoxido/di- $\mu$ -syn-syn pivalato pathway shows a much weaker magnetic coupling, as expected. Nevertheless, more examples of well magneto-structural characterized oxygen-bridged Gd<sub>n</sub> complexes are needed to confirm the above assumption.

We have studied the magnetothermal properties of **3** and **4** because 1) the magnetic interactions between the Gd<sup>3+</sup> ions are relatively weak for both compounds; 2) the Gd<sup>3+</sup> ion shows negligible anisotropy due to the absence of orbital contribution; 3) the Gd<sup>3+</sup> exhibits the largest single-ion spin ( $S_{Gd}$ = 7/2) arising from the 4f<sup>7</sup> electron configuration. These characteristics are known to favor a large MCE,<sup>[3a]</sup> that is, the change of the magnetic entropy ( $\Delta S_m$ ) following a change of the applied field. The entropy changes that characterize **3** and **4** can be calculated straightforwardly from the experimental heat capacity, *C*, (the Supporting Information, Figure S7) after obtaining the entropy according to the following expression:

$$S(T,B) = \int_{0}^{T} \frac{C(T,B)}{T} dT$$

Likewise,  $\Delta S_m$  can also be calculated from the magnetization data (the Supporting Information, Figure S9) by making use of the Maxwell relation:

$$\Delta S_{\rm m} = (T, \Delta B) = \int_{B_{\rm i}}^{B_{\rm f}} \left[ \frac{\partial M(T, B)}{dT} \right]_{B} dB$$

in which  $B_i$  and  $B_f$  are the initial and final applied magnetic fields. Figure 11 shows the dependence of  $-\Delta S_m$  on tempera-



Figure 11. The dependence of the magnetic entropy change on temperature and selected applied field changes, for 3 (a) and 4 (b), as obtained from heat capacity and magnetization data.

ture and applied field changes for both compounds. Note the nice agreement between the results obtained through both methods, thus validating the approaches employed. For the largest applied field change  $\Delta B = 7$  T, the maximum value of  $-\Delta S_m$  is 26.6 J kg<sup>-1</sup>K<sup>-1</sup> at T = 2.2 K for **3** and 27.1 J kg<sup>-1</sup>K<sup>-1</sup> at T = 2.4 K for **4**. Under our experimental conditions, the weak though not negligible antiferromagnetic interactions between the Gd<sup>3+</sup> ions inhibit  $-\Delta S_m(T,\Delta B)$  to attain the maximum entropy value per mole involved, that is,  $nRln(2S_{Gd} + 1) = 20.8 R = 29.7 J kg^{-1} K^{-1}$  for **3** and  $10.4 R = 35.4 J kg^{-1} K^{-1}$  for **4**. Finally, the so-obtained  $-\Delta S_m$  values for  $\Delta B = 7$  T are similar to those found for other Gd<sub>5</sub> and Gd<sub>10</sub> complexes, but lower than those found for other magnetically denser Gd<sub>n</sub> polynuclear complexes.<sup>(15)</sup> The results for **3** and **4** suggest that these systems can be used as molecular magnetic refrigerants.

As for the Dy<sup>3+</sup> (**1** and **6**) and Tb<sup>3+</sup> (**2** and **5**) complexes, the  $\chi_{\rm M}T$  product steadily decreases down to 2 K, which is due to the depopulation of the excited  $m_j$  sublevels of the Dy<sup>3+</sup> and Tb<sup>3+</sup> ions. This behavior arises from the splitting of the <sup>6</sup>H<sub>15/2</sub> and <sup>7</sup>F<sub>6</sub> ground terms, respectively, by the ligand field, and/or possible very weak intermolecular interactions between the Ln<sup>3+</sup> ions.

The field dependence of the magnetization for the  $Dy^{3+}$  and  $Tb^{3+}$  complexes is given in Figure 10. The *M* versus *H* plot at 2 K for these complexes shows a relatively rapid increase in the magnetization at low field to reach almost the saturation for magnetic fields of 5 T. The observed values at 5 T are rather lower than expected, which is due to crystal-field effects leading to significant magnetic anisotropy.<sup>[16]</sup>

Dy<sup>3+</sup> complexes are good candidates to exhibit SMM behavior because: 1) Dy<sup>3+</sup> is a Kramers ion and therefore the ground state bistability is guaranteed; 2) it has a large moment  ${}^{6}H_{15/2}$ spin orbit ground component, and 3) the f electronic cloud is largely anisotropic with an oblate shape, which can be stabilized by an axial crystal field that minimizes the repulsive interactions between the ligands and f-electron charge cloud.<sup>[17]</sup> Because the axial ligand field can be easily attained by serendipity in low symmetry Dy<sup>3+</sup> complexes, easy-axis anisotropy of the ground state and consequently SMM behavior is often observed for these complexes. In view of the above considerations, the low symmetry DyO<sub>7</sub>N and DyO<sub>8</sub> coordination environments observed for 1 and 6 could lead to SMM behavior. To know if compounds containing  $Dy^{3+}$  (1 and 6) and  $Tb^{3+}$  (2 and 5) exhibit slow relaxation of the magnetization and SMM behavior, alternating current (ac) magnetic susceptibility measurements as a function of the temperature and frequency were performed under zero and with small applied magnetic dc fields. The results of these measurements demonstrate that only compound 6 exhibits frequency dependence of the outof-phase  $(\chi_{M}^{*})$  signals under zero dc field and therefore slow relaxation and probably SMM behavior (Figure 12).

However, no maxima are observed in the temperature dependence of  $\chi''_{\rm M}$  above 2 K at frequencies reaching 1500 Hz, which does not allow us to extract the value of the thermal ac-



Figure 12. In-phase  $(\chi'_{M})$  and out-of-phase  $(\chi''_{M})$  signals under zero dc field for 6.

Chem. Eur. J. 2015, 21, 16955 - 16967



tivated energy barrier for the relaxation of the magnetization. When the ac measurements were performed in the presence of a small external dc field in the range 1000-4000 Oe, to fully or partly suppress the possible fast quantum tunneling relaxation, the temperature dependence of  $\chi''_{M}$  for **6** did not significantly change with field. However, compound 1 shows a clear frequency dependence the out-of-phase ( $\chi''_{M}$ ) signals below  $\approx$  10 K under a  $H_{dc}$  = 2000 Oe, typical of thermally activated relaxation process (the Supporting Information, Figure S9). The  $\chi''_{\rm M}$  signals are broad with maxima in the 6.75 (1488 Hz)–5.22 K (280 Hz) range and a tail below  $\approx\!4$  K ( $\chi^{\prime\prime}_{_{\rm M}}$  does not go to zero below the maxima but increases up to 2 K). This can be attributed to overlapping of different relaxation processes, including a faster quantum tunneling relaxation, which is responsible of the low temperature tail. The presence of five crystallographically independent Dy<sup>3+</sup> ions in the structure with very close DyO<sub>8</sub> coordination environments could be responsible for the existence of different overlapping thermally activated relaxation processes. It is worth noting that even two single-ion relaxation processes have been observed for complexes containing crystallographically equivalent  $Dy^{3+}$  sites.<sup>[16]</sup> At  $H_{dc} = 0.4 \text{ T}$ the quantum tunneling of magnetization (QTM) is almost suppressed (the tail at low temperature almost disappears) and the high temperature peaks remain roughly at the same temperatures as those observed under 0.2 T dc applied field but exhibit lower intensity (Figure 13). The fact that magnetic fields



Figure 13. In-phase  $(\chi'_{M})$  and out-of-phase  $(\chi''_{M})$  signals under 0.4 T dc field and Arrhenius plot for 1.

as high as 0.4 T are not able to fully eliminate the QTM relaxation process suggests that the remaining QTM process has its origin in hyperfine and intramolecular/intermolecular magnetic interactions.

The Cole–Cole diagram in the temperature range 4.8 K (the Supporting Information, Figure S10) exhibits semicircular shapes that can be fitted using the generalized Debye model. This affords  $\alpha$  values in the range 0.55–0.64, which support the

existence of a broad distribution of relaxation times. The fit of the frequency dependence of  $\chi''_{M}$  at each temperature to the generalized Debye model allowed us to extract the relaxation time  $\tau$  at different temperatures. The results were then used to construct the Arrhenius plot shown in Figure 13. The linear fit of the data ( $\tau$  vs. 1/T) afforded an effective energy barrier for the reversal of the magnetization of 16.12(8) K with  $\tau_o$  = 3.3× 10<sup>-5</sup> s. The  $\tau_o$  value is still larger than that usually observed for pure thermally activated processes (typical values are found in the 10<sup>-7</sup>–10<sup>-10</sup> s range), thus supporting that the QTM has not been fully suppressed after the application of a dc field of 0.4 T, which could be due to hyperfine and intermolecular interactions. It is worth mentioning that the extracted  $\tau_o$  value for 1 is similar to the values previously reported for a large number of Dy clusters in the same temperature range.<sup>[12c,18]</sup>

The fast relaxation of the magnetization observed for compounds **1** and **6**, even in the presence of applied magnetic field, could be due to quantum tunneling leading to apparently lower  $U_{eff}$  values. It has been recently proposed from theoretical and experimental studies on a dinuclear  $Dy_2$  complex<sup>[19]</sup> that Dy···Dy intramolecular magnetic exchange interactions in polymetallic  $Dy^{3+}$  complexes have the effect of quenching the SMM behavior when the anisotropic axis of the  $Dy^{3+}$  ions are not parallel. In complex **1** with a  $Dy_{10}$  wheel structure, as well as in compound **6**, whose structure is made of two vertex-sharing  $Dy_3$  triangles turned away from each other, in principle, the principal anisotropic axes could not be parallel and therefore the Ln···Ln interactions could reduce the barrier to magnetization reversal.

Although the Dy<sup>III</sup> ions in 1 are not strictly in the same plane (they are located alternatively 0.57 Å above and below the plane), the structure is centrosymmetric and, therefore, the anisotropic axes on opposite Dy centers, if they exist, would be parallel but having opposite senses. This result, together with the antiferromagnetic interaction between the Dy<sup>III</sup> ions, might generate a net quasi-toroidal moment for the projections of the local magnetic moments on to the plane of the wheel. Ab initio calculations are planned for the near future to determine if compound 1 is a SMT.

## Conclusion

The present work describes the synthesis, structures, and magnetic properties of decanuclear  $Ln_{10}$  as well as pentanuclear  $Ln_5$  complexes by using a multisite coordination ligand (LH<sub>3</sub>). The formation of  $Ln_{10}$  and  $Ln_5$  complexes are fully governed by the stoichiometry of the regents used. The dynamic magnetic studies for complex 1 show the SMM behavior with the following characteristics:  $U_{eff} = 16.12(8)$  K and  $\tau_0 = 3.3 \times 10^{-5}$  s under 0.4 T dc field. However, complex **6** shows the frequency dependent maxima in the out-of-phase signal under zero dc field, without achieving maxima above 2 K. Complexes **3** and **4** show a significant magnetocaloric effect with the following characteristic values:  $-\Delta S_m = 26.6 \text{ J kg}^{-1} \text{ K}^{-1}$  at T = 2.2 K for **3** and  $-\Delta S_m = 27.1 \text{ J kg}^{-1} \text{ K}^{-1}$  at T = 2.4 K for **4**, both for an applied field change of 7 T.



## **Experimental Section**

#### Reagents and general procedures

Solvents and other general reagents used in this work were purified according to standard procedures.<sup>[20]</sup> 2,6-Bis(hydroxymethyl)-4-methylphenol, activated manganese (IV) dioxide (MnO<sub>2</sub>), [DyCl<sub>3</sub>]· $6H_2O$ , [TbCl<sub>3</sub>]· $6H_2O$ , [HoCl<sub>3</sub>]· $6H_2O$ , and [GdCl<sub>3</sub>]· $6H_2O$  were obtained from Sigma Aldrich Chemical Co. and were used as received. 2-Amino ethanol and sodium sulfate (anhydrous) were obtained from S.D. Fine Chemicals, Mumbai, India, and were used as received. 2-(Hydroxymethyl)-6-carbalde-hyde-4-methylphenol was prepared according to a literature procedure.<sup>[11a]</sup>

#### Instrumentation

Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating at 400–4000 cm<sup>-1</sup>. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model.

#### Magnetic measurements

Field dependence of the magnetization at different temperatures and variable temperature (2–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at different magnetic fields. Alternating current (ac) susceptibility measurements were performed using an oscillating ac field of 3.5 Oe and ac frequencies ranging from 1 to 1500 Hz. The experimental susceptibilities were corrected for the sample holder and diamagnetism of the constituent atoms by using Pascal's tables. A pellet of the sample cut into very small pieces was placed in the sample holder to prevent any torqueing of the microcrystals.

#### Heat capacity measurements

The heat capacity measurements for **3** and **4** were carried out for temperatures down to 0.3 K by using a Quantum Design 9T-PPMS, equipped with a <sup>3</sup>He cryostat. The experiments were performed on thin pressed pellets (ca. 1 mg) of a polycrystalline sample, thermalized by about 0.2 mg of Apiezon N grease, whose contribution was subtracted by using a phenomenonological expression.

## X-ray crystallography

Single crystals of **1–6** were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with a CRYO Industries low-temperature apparatus and intensity data were collected using graphitemonochromated Mo<sub>Kα</sub> radiation ( $\lambda = 0.71073$  Å). The program SMART<sup>[21a]</sup> was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT<sup>[21a]</sup> for integration of the intensity of reflections and scaling, SADABS<sup>[21b]</sup> for absorption correction, and SHELXTL<sup>[21c,d]</sup> for space group and structure determination and least-squares refinements on F<sup>2</sup>. All the structures were solved by direct methods using the program SHELXS-97<sup>[21e]</sup> and refined by full-matrix least-squares methods against F<sup>2</sup> with SHELXL-97.<sup>[21e]</sup> Hydrogen atoms were fixed at calculated positions

Table 3. Crystal data and structure refinement parameters of 1–3.					
	1	2	3		
formula M g <sup>-1</sup> crystal system	$C_{177}H_{241}CI_{27}Dy_{10}N_{14}O_{50}$ 5946.99 triclinic	C <sub>176</sub> H <sub>240</sub> Cl <sub>24</sub> N <sub>14</sub> O <sub>50</sub> Tb <sub>1</sub> 5791.82 triclinic	C <sub>176</sub> H <sub>240</sub> Cl <sub>24</sub> Gd <sub>10</sub> N <sub>14</sub> O <sub>53</sub> 5823.11 triclinic		
space group	ΡĪ	ΡĪ	ΡĪ		
a [Å]	22.0177(11)	22.0256(15)	22.112(2)		
b [Å]	23.0226(11)	23.0524(15)	23.103(2)		
c [Å]	24.8075(12)	24.7831(17)	24.886(2)		
α [°]	63.2250(10)	63.3580(10)	63.227(2)		
β [°]	83.5980(10)	83.503(2)	83.387(2)		
γ [°]	82.6300(10)	82.659(2)	82.508(2)		
V [ų]	11113.5(9)	11133.1(13)	11 230.6(19)		
Ζ	2	2	2		
$ ho_{ m c}$ [g cm $^{-3}$ ]	1.777	1.728	1.722		
$\mu  [mm^{-1}]$	3.714	3.491	3.267		
F(000)	5840	5704	5732		
cryst size [mm <sup>3</sup> ]	0.067×0.043×0.033	$0.035 \times 0.021 \times 0.016$	0.035×0.026×0.016		
$\theta$ range [deg]	2.00 to 25.50	4.08 to 25.03	4.09 to 19.55		
limiting indices	-26 < = h < = 24	-26 < = h < = 25	-20 < = h < = 20		
	-27 < = k < = 27	-25 < = k < = 27	-21 < = k < = 18		
	-30 < = l < = 29	-29 < = l < = 29	-23 < = l < = 22		
refins collected	80704	74945	40633		
independent reflns	41251[R(int)=0.0326]	38974	19255 [R <sub>int</sub> =0.0581,		
		[ <i>R</i> (int) = 0.0572]	R <sub>sigma</sub> = 0.0799]		
completeness to $\theta$ [%]	99.7	99.1	98.8		
refinement	full-matrix-block	full-matrix-block	full-matrix-block		
method	least-squares on F <sup>2</sup>	least-squares on F <sup>2</sup>	least-squares on F <sup>2</sup>		
data/restraints/pa- rameters	41251/44/2575	38974/46/2526	19255/606/2556		
goodness-of-fit on F <sup>2</sup>	1.016	1.025	1.044		
final R indices	$R_1 = 0.0368$ ,	$R_1 = 0.0576$ ,	$R_1 = 0.0590,$		
$[l > 2\theta(l)]$	$wR_2 = 0.0832$	$wR_2 = 0.1360$	$wR_2 = 0.1591$		
R indices (all data)	$R_1 = 0.0572,$	$R_1 = 0.0904$	$R_1 = 0.0742,$		
	$wR_2 = 0.0914$	$wR_2 = 0.153$	$wR_2 = 0.1719$		
largest diff. peak and hole [eÅ <sup>-3</sup> ]	3.602 and -1.606	4.830 and -1.694	4.22 and -1.32		

and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Non-positive definite atoms present in compound **3** were treated with ISOR restraints and refined using the Olex-2 software.<sup>[21f]</sup> The crystallographic figures have been generated using Diamond 3.1e software.<sup>[21g]</sup> The crystal data and the cell parameters for compounds **1–6** are summarized in Tables 3 and 4. CCDC 1401022 (**1**), 1401023 (**2**), 1401024 (**3**), 1401025 (**4**), 1401026 (**5**), and 1401027 (**6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

## **Syntheses**

(E)-2-((2-Hydroxyethylimino)methyl)-6-(hydroxymethyl)-4-meth-

**ylphenol** (LH<sub>3</sub>): 2-Amino ethanol (0.37 g, 6.07 mmol) dissolved in dry methanol (10 mL) was added dropwise over a period of 10 min to a stirred solution of **C2** (1.01 g, 6.07 mmol) in dry methanol (20 mL). The resulting reaction mixture was heated under reflux for 4 h. Then, the reaction mixture was cooled to room temperature. Thereafter the solvent was concentrated in vacuum to 10 mL and kept in a refrigerator at 0 °C for 2 h to obtain a bright-yellow crystalline solid, which was further suction-filtered, washed with a small amount of cold methanol, and air-dried. Yield: 1.06 g,

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16964



Table 4. Crystal data and structure refinement parameters of 4–6.					
	4	5	6		
formula	C <sub>81</sub> H <sub>129</sub> Gd <sub>5</sub> N <sub>4</sub> O <sub>31</sub>	C <sub>79</sub> H <sub>123</sub> N <sub>4</sub> O <sub>30</sub> Tb <sub>5</sub>	C <sub>81</sub> H <sub>127</sub> Dy <sub>5</sub> N <sub>4</sub> O <sub>30</sub>		
ing	Z441.15	2403.41	2449.57 monoclinic		
space group	PZ <sub>1</sub> 14 410(5)	Γ2 <sub>1</sub> 14 292(Ε)	$PZ_1$		
u [A]	14.419(5)	14.202(5)	14.445(5)		
	23.412(J) 16.097(E)	22.202(5) 1E 97E(E)	25.212(5)		
	10.007(5)	13.073(3)	13.903(3)		
μ[] ν[Å <sup>3</sup> ]	115.207(5)	110.074(5)	114.040(5)		
V [A ]	4910(3)	4703(2)	4888(3)		
2 a [a cm <sup>-3</sup> ]	2	2	1 661		
$p_{c}$ [g cm ]	2.405	1.097	1.004		
$\mu$ [mm]	3.403 2422	5./80 2290	3.849 2422		
F(000)			2422		
Crystal size [mm]	0.044 × 0.021 × 0.015	0.062 × 0.037 × 0.024	0.058 × 0.058 × 0.021		
limiting indices	4.12 10 23.03	4.11 10 25.05	4.10 10 25.05		
limiting indices	-17 < = 11 < = 17	-17 < = 11 < = 14	-17 < = 11 < = 11		
	$-27 \leq -16$	-20 < = k < = 20	-27 < = K < = 27		
roflag colloctor	-19 < =1 < =10	-14 < = 1 < = 18	-17 < =1 < =19		
independent rofins	3377Z	31223	32 333		
independent reins	1/214	[D(int) 0.02(0]	[D(int) 0.0440]		
	[R(IRI) = 0.0478]	[R(Int) = 0.0508]	[R(IIII) = 0.0449]		
completeness to $\theta$ [%]	99.5 full mantrix logat	99.5 full matrix logat	99.4 full matrix logat		
rennement method	ruii-matrix least-	$r_{2}$	ruii-matrix ieast-		
data /vostvoints /navanas	squares on F	squares on F	squares on F		
uala/restraints/params	1/214/30/1094	10993/10/1044	10934/12/1113		
goodness-of-fit on F	1.034	1.029 D 0.0204	1.019 D 0.0425		
	$R_1 = 0.0508,$	$R_1 = 0.0394,$	$K_1 = 0.0435,$		
[I > ZU(I)]	$WR_2 = 0.1098$	$wn_2 = 0.0834$	$W\pi_2 = 0.1053$		
r indices (all data)	$\pi_1 = 0.06/2,$	$\kappa_1 = 0.0502,$	$\kappa_1 = 0.0524,$		
largest diff post	$wn_2 = 0.1160$	$WR_2 = 0.08/3$	$W\pi_2 = 0.1090$		
hole [eÅ <sup>-3</sup> ]	1.536 and -1.302	2.250 and -1.451	1.724 and -1.070		
flack parameter	0.010(13)	-0.003(10)	0.013(11)		

83.5%. M.p. 95°C; H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.51 (s, 1 H, imino), 7.59 (s, 1 H, Ar-H), 7.24 (s, 1 H, Ar-H), 4.71 (s, 2 H, CH<sub>2</sub>OH), 3.90 (t, 2 H, CH<sub>2</sub>), 2.85 (t, 2 H, CH<sub>2</sub>), 1.29 ppm (s, 3 H, CH<sub>3</sub>); FTIR (KBr):  $\tilde{\nu}$  = 3309 (b), 2975 (m), 2865 (m), 1635 (s), 1460 (s), 1360 (w), 1264 (s), 1090 (w), 1074 (s), 971 (w), 864 (s) cm<sup>-11</sup>; elemental analysis calcd (%) for C<sub>11</sub>H<sub>15</sub>NO<sub>3</sub> (209.2417): C 63.14, H 7.23, N 6.69; found: C 63.21, H 7.28, N 6.72.

General synthetic procedure for the preparation of complexes 1–3: A general procedure was used for the preparation of these complexes (1–3).  $[LnCl_3]$ -6H<sub>2</sub>O (0.28 mmol) was added to a solution of LH<sub>3</sub> (0.06 g, 0.28 mmol) in methanol (5 mL), and the reaction mixture was stirred at room temperature for 5 min. Then, subsequently triethylamine (0.08 g, 0.84 mmol) and pivalic acid (PivH) (0.03 g, 0.28 mmol) were added dropwise to this stirring solution. Then, the solution was stirred for a further period of 2 h at room temperature to afford a light-yellow precipitate that was filtered and washed with cold methanol (2 mL). Then this precipitate redissolved in 10 mL of acetonirile/chloroform (1:1) solvent mixture and kept for crystallization in slow evaporation. After about one week, block-shaped, colorless crystals, suitable for X-ray crystallography were obtained. Specific details of each reaction and the characterization data of the products obtained are given below.

 [**Tb**<sub>10</sub>(**LH**)<sub>10</sub>(**κ**<sup>2</sup>-**Piv**)<sub>10</sub>]-8 **CHCl**<sub>3</sub>-4 **CH**<sub>3</sub>**CN** (2): Quantities: LH<sub>3</sub> (0.06 g, 0.28 mmol), [TbCl<sub>3</sub>]-6 H<sub>2</sub>O (0.10 g, 0.28 mmol), Et<sub>3</sub>N (0.08 g, 0.84 mmol), PivH (0.03 g, 0.28 mmol). Yield: 0.082 g, 51% (based on Tb). Mp: 149 °C (d); IR (KBr):  $\tilde{\nu} =$ 3125 (b), 2958 (w), 2917 (w), 2826 (w), 1643 (s), 1556 (s), 1541 (s), 1481 (s), 1449 (s), 1363 (s), 1260 (s), 1224 (w), 1174 (w), 1067 (s), 972 (w), 898 (w), 805 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>176</sub>H<sub>240</sub>Cl<sub>24</sub>N<sub>14</sub>O<sub>50</sub>Tb<sub>10</sub> (5791.96): C 36.50, H 4.18, N 3.39; found: C 36.72, H 4.25, N 3.40.

[**Gd**<sub>10</sub>(**LH**)<sub>10</sub>(**κ**<sup>2</sup>-**Piv**)<sub>10</sub>]-8 **CHCl**<sub>3</sub>-4 **CH**<sub>3</sub>**CN**-3**H**<sub>2</sub>**O** (3): Quantities: LH<sub>3</sub> (0.06 g, 0.28 mmol), [GdCl<sub>3</sub>]-6 H<sub>2</sub>O (0.10 g, 0.28 mmol), Et<sub>3</sub>N (0.08 g, 0.84 mmol), PivH (0.03 g, 0.28 mmol). Yield: 0.043 g, 26% (based on Gd); M.p. 151 °C (d); IR (KBr):  $\tilde{\nu} = 3122$  (b), 2960 (w), 2921 (w), 2828 (w), 1643 (s), 1547 (s), 1531 (s), 1485 (s), 1428 (s), 1358 (s), 1263 (s), 1220 (w), 1174 (w), 1087 (s), 972 (w), 897 (w), 803 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>176</sub>H<sub>240</sub>Cl<sub>24</sub>Gd<sub>10</sub>N<sub>14</sub>O<sub>53</sub> (5823.11): C 36.3, H 4.15, N 3.36; found: C 36.01, H 4.18, N 3.24.

General synthetic procedure for the preparation of the complexes 4–6: All the metal complexes (4–6) were synthesized according to the following procedure. LH<sub>3</sub> (0.06 g, 0.28 mmol) was dissolved in methanol (10 mL). [LnCl<sub>3</sub>]·6H<sub>2</sub>O (0.35 mmol) was added to this solution and the reaction mixture was stirred at room temperature for 10 min. At this stage excess triethylamine (0.14 g, 1.40 mmol) was added dropwise to this solution. Within few minutes, the solution was getting turbid. Then, pivalic acid (PivH) (0.057 g, 0.56 mmol) was added to the mixture and was stirred for a further period of 8 h at room temperature to afford a clear yellow solution,

which was filtered and kept for crystallization in slow evaporation. After about one week, block-shaped, colorless crystals, suitable for X-ray crystallography were obtained. Specific details of each reaction and the characterization data of the products obtained are given below.

 $\begin{bmatrix} \mathbf{Gd}_{5}(\mathbf{LH})_{4}(\boldsymbol{\mu}_{2}-\boldsymbol{\eta}^{1}\boldsymbol{\eta}^{1}\mathbf{Piv})_{4}(\boldsymbol{\eta}^{1}\mathbf{Piv})_{3}(\mathbf{CH}_{3}\mathbf{OH})\end{bmatrix} \cdot \mathbf{CH}_{3}\mathbf{OH} \cdot \mathbf{3H}_{2}\mathbf{O} \quad (4): \quad \text{Quantities: LH}_{3} (0.06 \text{ g}, 0.28 \text{ mmol}), \quad \begin{bmatrix} \mathbf{GdCI}_{3} \cdot \mathbf{6H}_{2}\mathbf{O} (0.13 \text{ g}, 0.35 \text{ mmol}), \quad \mathbf{Et}_{3}\mathbf{N} \\ (0.14 \text{ g}, 1.40 \text{ mmol}), \quad \mathbf{PivH} \quad (0.057 \text{ g}, 0.56 \text{ mmol}). \quad \mathbf{Yield:} \quad 0.095 \text{ g}, \\ 55.59\% \text{ (based on Gd). M.p. 230 °C (d); IR (KBr): } \tilde{\nu} = 3397 \text{ (b), } 2955 \\ (s), 2677 (w), 1648 (s), 1581(s), 1538 (s), 1453 (s), 1374 (s), 1308 (s), \\ 1226 (s), 1178 (w), 1044 (s), 1018 (s), 976 (w), 898 (s), 863 \text{ cm}^{-1} (w); \\ \text{elemental analysis calcd (\%) for } C_{81}H_{129} \text{ Gd}_{5}N_{4}O_{31} (2441.14): C 39.85, \\ \text{H} 5.33, \text{N} 2.30; \text{ found: C } 40.03, \text{H} 5.38, \text{N} 2.43. \\ \end{bmatrix}$ 

[**Tb**<sub>5</sub>(**LH**)<sub>4</sub>(**μ**<sub>2</sub>-**η**<sup>1</sup>**η**<sup>1</sup>**Piv**)<sub>4</sub>(**η**<sup>1</sup>**Piv**)<sub>3</sub>(**H**<sub>2</sub>**O**)]-3 **H**<sub>2</sub>**O** (5): Quantities: LH<sub>3</sub> (0.06 g, 0.28 mmol), [TbCl<sub>3</sub>]-6 H<sub>2</sub>O (0.13 g, 0.35 mmol), Et<sub>3</sub>N (0.14 g, 1.40 mmol), PivH (0.057 g, 0.56 mmol). Yield: 0.102 g, 60.62% (based on Tb). M.p. 230 °C (d); IR (KBr):  $\tilde{\nu} = 3390$  (b), 2955 (s), 2676 (w), 1649 (s), 1584 (s), 1539 (s), 1454 (s), 1374 (s), 1303 (s), 1227 (s), 1177 (w), 1046 (s), 1018 (s), 977 (w), 897 (s), 863 cm<sup>-1</sup> (w); elemental analysis calcd (%) for C<sub>79</sub>H<sub>123</sub>N<sub>4</sub>O<sub>30</sub>Tb<sub>5</sub> (2403.47): C 39.48, H 5.16, N 2.33; found: C 39.67, H 5.25, N 5.41.

 $[Dy_{5}(LH)_{4}(\mu_{2}-\eta^{1}\eta^{1}Piv)_{4}(\eta^{1}Piv)_{3}(H_{2}O)]\cdot CH_{3}OH\cdot 2H_{2}O \ \ (6): \ \ Quantities:$  $LH_{3} (0.06 g, 0.28 mmol), [DyCl_{3}]\cdot 6H_{2}O (0.13 g, 0.35 mmol), Et_{3}N (0.14 g, 1.40 mmol), PivH (0.057 g, 0.56 mmol). Yield: 0.099 g,$  $57.74% (based on Dy). M.p. 230 °C (d); IR (KBr): <math>\tilde{\nu} = 3388$  (b), 2956 (s), 2666 (w), 1649 (s), 1586 (s), 1541 (s), 1454 (s), 1360 (s), 1304 (s), 1226 (s), 1178 (w), 1048 (s), 1018 (s), 977 (w), 899 (s), 860 cm<sup>-1</sup> (w);

Chem. Eur. J. 2015, 21, 16955 - 16967

www.chemeurj.org

16965



elemental analysis calcd (%) for  $C_{81}H_{127}$  Dy\_5N4O\_30 (2449.38): C 39.72, H 5.23, N 2.29; found: C 39.79, H 5.31, N 2.35.

## Acknowledgements

We are thankful to the Department of Science and Technology, New Delhi, for financial support. S.D., A.D., S.K., and S.B. thank CSIR, India for Senior Research Fellowship. V.C. is thankful to the Department of Science and Technology for a J. C. Bose National Fellowship. EC is thankful for financial support to Ministerio de Economía y Competitividad (MINECO) for Projects CTQ-2011-24478, CTQ2014-56312-P, the Junta de Andalucía (FQM-195 and the Project of excellence P11-FQM-7756), the University of Granada financial support. M.E. acknowledges financial support from MINECO through grant MAT2012-38318-C03-01. ST thanks the Junta de Andalucía for a postdoctoral contract.

**Keywords:** lanthanide complexes · ligands · macrocycles · magnetic properties · X-ray diffraction

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Chem. Eur. J. 2015, 21, 16955 - 16967



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Received: May 21, 2015 Published online on September 30, 2015