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Molecular Magnets Based on Homometallic Hexanuclear Lanthanide(III) Complexes

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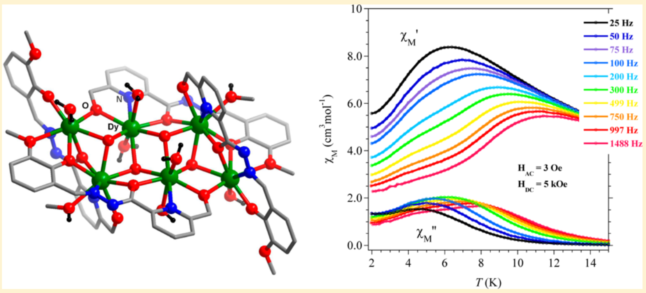
Supporting Information

ABSTRACT: The reaction of lanthanide(III) chloride salts (Gd(III), Dy(III), Tb(III), and Ho(III)) with the hetero donor chelating ligand *N*′-(2-hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl)picolinohydrazide (LH$_3$) in the presence of triethylamine afforded the hexanuclear Ln(III) complexes $[\{Ln_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_p[H_2O]_q[Cl]_4\cdot xH_2O\cdot yCH_3OH$ (**1**, Ln = Gd(III), $p = 4$, $q = 4$, $x = 8$, $y = 2$; **2**, Ln = Dy(III), $p = 2$, $q = 6$, $x = 8$, $y = 4$; **3**, Ln = Tb(III), $p = 2$, $q = 6$, $x = 10$, $y = 4$; **4**, Ln = Ho(III), $p = 2$, $q = 6$, $x = 10$, $y = 2$). X-ray diffraction studies revealed that these compounds possess a hexanuclear $[Ln_6(OH)_4]^{14+}$ core consisting of four fused $[Ln_3(OH)]^{8+}$ subunits. Both static (dc) and dynamic (ac) magnetic properties of **1**−**4** have been studied. Single-molecule magnetic behavior has been observed in compound **2** with an effective energy barrier and relaxation time pre-exponential parameters of $\Delta/k_B = 46.2$ K and $\tau_0 = 2.85 \times 10^{-7}$ s, respectively.



■ INTRODUCTION

For the past two decades, the chemistry of lanthanide complexes has experienced a renaissance of sorts in view of the new applications of these complexes in catalysis,[1] luminescent materials,[2] and magnetic materials.[3] In the field of molecular magnetism in general and single-molecule magnets (SMMs) in particular, heterometallic 3d/4f[4] and homometallic 4f[3,5] complexes have made a substantial impact, owing to the large ground-state spin of lanthanide ions and also to their substantial magnetic anisotropy.[6] In fact, some of the largest energy barriers known for the reversal of magnetization among single-molecule magnets are displayed by polynuclear lanthanide complexes, as exemplified by $\{Dy_5\}$[7] and $\{K_2Dy_4\}$[8] complexes. The magnetic anisotropy of lanthanide ions have also rendered them as suitable candidates in single-ion magnets (SIMs).[9]

We have utilized the phosphorus-supported hydrazone ligand $S{=}P[N(Me)N{=}CH\text{-}C_6H_3\text{-}2\text{-}OH\text{-}3\text{-}OMe]_3$ and have prepared several heterometallic 3d/4f[10] complexes, many of which have been shown to be SMMs; notably we also were able to demonstrate the first example of $Co^{II}_2Ln^{III}$[10a,b] SMMs. Spurred by this, we have been examining other systems including polynuclear lanthanide complexes. Thus, we have recently reported a tetranuclear compound, $[\{(L'H)_2Dy_4\}(\mu_2\text{-}O)_4](H_2O)_8\cdot 2CH_3OH\cdot 8H_2O$ (L′H$_3$ = 6-(hydroxymethyl)-*N*′-((8-hydroxyquinolin-2-yl)methylene)picolinohydrazide),[11] which possesses a rhombus-type geometry and shows a double relaxation in its dynamic magnetization studies. Exploiting the concept of keto−enol tautomerism and conformational flexibility of ligands, a concept introduced by Tang and coworkers,[19b] we prepared the series of tetranuclear derivatives $[Ln_4(LH)_2(LH_2)_2(\mu_2\text{-}\eta^1\eta^1\text{-}Piv)_2(\eta^1\text{-}Piv)_4]\cdot 2CHCl_3$[12] ($Ln^{III}$ = Dy, Tb, Gd; LH$_3$ = *N*′-(2-hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl)picolinohydrazide), in which the Dy^{III} derivative was shown to possess a SMM behavior with a two-step relaxation. In a continuation of these studies, we now reveal the assembly of hexanuclear lanthanide $\{Ln_6\}$ complexes (Ln(III) = Gd (**1**), Dy (**2**), Tb (**3**), Ho (**4**)), prepared by using LH$_3$. Among these compounds, **2** is shown to possess slow relaxation of magnetization below 14 K. These results are discussed herein.

■ EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.[13] Pyridine-2,6-dicarboxylic acid, sodium borohydride, $DyCl_3\cdot 6H_2O$, $TbCl_3\cdot 6H_2O$, $GdCl_3\cdot 6H_2O$, and $HoCl_3\cdot 6H_2O$ were

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Table 1. Crystal Data and Structure Refinement Parameters of 1−4

	1	2	3	4
formula	$C_{66}H_{102}Cl_4Gd_6N_{12}O_{38}$	$C_{66}H_{98}Cl_4Dy_6N_{12}O_{40}$	C_{66} $H_{96}Cl_4Tb_6N_{12}O_{42}$	C_{64} $H_{100}Cl_4Ho_6N_{12}O_{40}$
formula wt	2756.90	2816.36	2824.87	2808.94
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.065(5)	12.042(5)	12.063(5)	12.059(5)
b (Å)	12.880(5)	12.905(5)	12.876(5)	12.920(5)
c (Å)	16.967(5)	16.891(5)	16.830(5)	16.840(5)
α (deg)	69.631(5)	68.012(5)	67.649(5)	68.218(5)
β (deg)	89.371(5)	88.667(5)	87.699(5)	88.492(5)
γ (deg)	76.267(5)	76.685(5)	76.692(5)	76.446(5)
V (Å^3)	2393.7(15)	2362.8(15)	2349.5(15)	2363.2(15)
Z	1	1	1	1
ρ_c (g cm^{-3})	1.913	1.979	1.997	1.974
μ (mm^{-1})	4.295	4.887	4.662	5.164
F(000)	1338	1362	1370	1358
cryst size (mm^3)	0.049 × 0.036 × 0.022	0.057 × 0.039 × 0.028	0.056 × 0.035 × 0.027	0.053 × 0.042 × 0.025
θ range (deg)	4.08−25.03	4.09−25.03	4.08−25.02	4.11−25.03
limiting indices	$-12 \leq h \leq +14$, $-15 \leq k \leq +13$, $-24 \leq l \leq +24$	$-14 \leq h \leq +14$, $-15 \leq k \leq +11$, $-20 \leq l \leq +19$	$-14 \leq h \leq +14$, $-15 \leq k \leq +15$, $-20 \leq l \leq +11$	$-10 \leq h \leq +14$, $-15 \leq k \leq +15$, $-17 \leq l \leq +20$
no. of rflns collected	12467	12431	12108	26983
no. of indep rflns	8282 (R(int) = 0.0254)	8205 (R(int) = 0.0510)	8098 (R(int) = 0.0246)	8108 (R(int) = 0.0413)
completeness to θ (%)	97.8	98.1	97.5	97.0
refinement method	full-matrix-block least squares on F^2			
no. of data/restraints/params	8282/38/588	8205/19/605	8098/28/601	8108/12/581
goodness of fit on F^2	1.090	1.047	1.034	1.101
final R indices ($I > 2\sigma(I)$)	R1 = 0.0542, wR2 = 0.1472	R1 = 0.0725, wR2 = 0.1691	R1 = 0.053, wR2 = 0.1471	R1 = 0.0471, wR2 = 0.1248
R indices (all data)	R1 = 0.0710, wR2 = 0.1685	R1 = 0.1127, wR2 = 0.2114	R1 = 0.0655, wR2 = 0.1653	R1 = 0.0643, wR2 = 0.1411
largest diff peak, hole (e Å^{-3})	2.840, −1.781	2.487, −4.034	3.306, −2.344	2.514, −2.064

obtained from Sigma-Aldrich and were used as received. *o*-Vanillin, hydrazine hydrate (80%), and sodium sulfate (anhydrous) were obtained from SD Fine Chemicals, Mumbai, India. Methyl-6-(hydroxymethyl)picolinate,[14,12] 6-(hydroxymethyl)-picolinohydrazide,[12] and *o*-vanillin 6-(hydroxymethyl)picolinoyl hydrazone (LH_3)[12] were prepared according to literature procedures.

General Synthetic Procedure for the Preparation of Complexes 1−4. All of the metal complexes (**1**−**4**) were synthesized according to the following procedure. LH_3 (0.06 g, 0.20 mmol) was dissolved in methanol (10 mL) and chloroform (5 mL). To this was added 1.5 equiv of $LnCl_3{\cdot}6H_2O$ (0.30 mmol). The reaction mixture was stirred at room temperature for 10 min. At this stage excess triethylamine (0.10 mL, 1 mmol) was added dropwise and the mixture was stirred for a further period of 10 h at room temperature to afford a clear yellow solution, which was filtered and kept for crystallization. After about 10 days, block-shaped, colorless crystals suitable for X-ray crystallography were obtained by slow evaporation from the solvent mixture. Specific details of each reaction and the characterization data of the products obtained are given below.

*$[\{Gd_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_4[H_2O]_4[Cl]_4{\cdot}8H_2O{\cdot}2CH_3OH$ (**1**).* LH_3 (0.060 g, 0.20 mmol), $GdCl_3{\cdot}6H_2O$ (0.111 g, 0.30 mmol), and Et_3N (0.1 mL, 1 mmol). Yield: 42 mg, 30% (based on Gd). Mp: 180 °C dec. IR (KBr, cm^{-1}): 3405 (b), 1613 (s), 1564 (s), 1544 (m), 1474 (s), 1443 (w), 1397 (m), 1366 (s), 1354 (m), 1239 (s), 1171 (m), 1077 (m), 1036 (s), 951 (m), 747 (s). Anal. Calcd for $C_{66}H_{102}Cl_4Gd_6N_{12}O_{38}$ (2756.90): C, 28.27; H, 3.73; N, 6.10. Found: C, 27.92; H, 3.41; N, 6.29.

*$[\{Dy_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_2[H_2O]_6[Cl]_4{\cdot}8H_2O{\cdot}4CH_3OH$ (**2**).* LH_3 (0.060 g, 0.20 mmol), $DyCl_3{\cdot}6H_2O$ (0.112 g, 0.30 mmol), and Et_3N (0.1 mL, 1 mmol). Yield: 55 mg, 39% (based on Dy). Mp: 178 °C dec. IR (KBr, cm^{-1}): 3394 (b), 1614 (s), 1570 (s), 1561 (w), 1462 (s), 1452 (s), 1371 (m), 1355 (s), 1309 (w), 1222 (s), 1177 (m), 1034 (s), 950 (m), 747(s). Anal. Calcd for $C_{66}H_{106}Cl_4Dy_6N_{12}O_{40}$ (2824.42): C, 28.07; H, 3.78; N, 5.95. Found: C, 27.81; H, 3.49; N, 6.23.

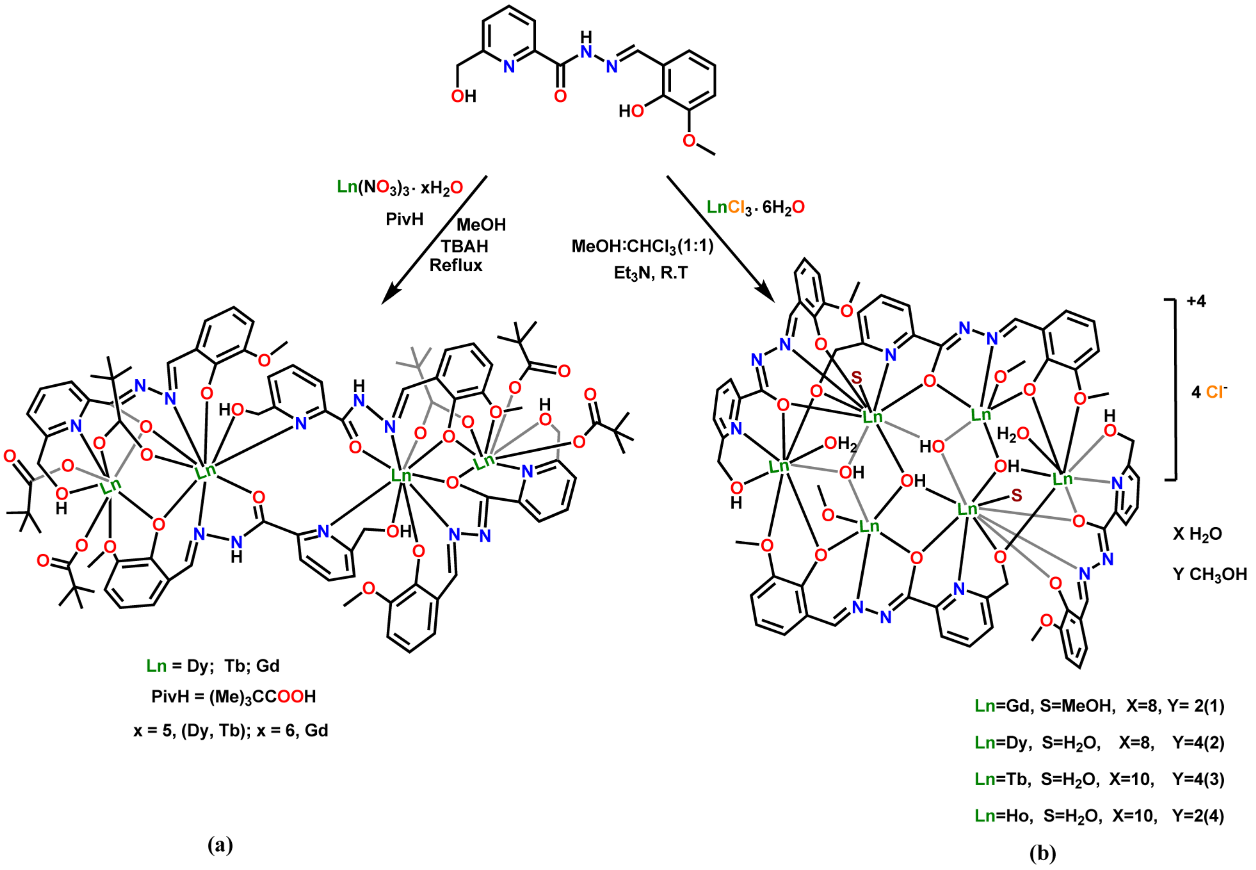
*$[\{Tb_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_2[H_2O]_6[Cl]_4{\cdot}10H_2O{\cdot}4CH_3OH$ (**3**).* LH_3 (0.060 g, 0.20 mmol), $TbCl_3{\cdot}6H_2O$ (0.111 g, 0.30 mmol) and Et_3N (0.1 mL, 1 mmol). Yield: 58 mg, 40% (based on Tb). Mp: 175 °C dec. IR (KBr, cm^{-1}): 3410 (w), 1612 (s), 1572 (s), 1558 (w), 1462 (s), 1453 (s), 1377 (m), 1351 (s), 1308 (w), 1239 (s), 1176 (m), 1035 (s), 951 (m), 747 (s). Anal. Calcd for $C_{66}H_{108}Cl_4Tb_6N_{12}O_{42}$ (2836.98): C, 27.94; H, 3.84; N, 5.92. Found: C, 27.85; H, 3.56; N, 6.25.

*$[\{Ho_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_2[H_2O]_6[Cl]_4{\cdot}10H_2O{\cdot}2CH_3OH$ (**4**).* LH_3 (0.060 g, 0.20 mmol), $HoCl_3{\cdot}6H_2O$ (0.113 g, 0.30 mmol) and Et_3N (0.1 mL, 1 mmol). Yield: 52 mg, 37% (based on Ho). Mp: 178 °C dec. IR (KBr, cm^{-1}): 3415 (w), 1613 (s), 1564 (s), 1544 (w), 1462 (s), 1453 (s), 1397 (m), 1354 (s), 1308 (w), 1239 (s), 1171 (m), 1036 (s), 950 (m), 747 (s). Anal. Calcd for $C_{64}H_{100}Cl_4Ho_6N_{12}O_{40}$ (2808.94): C, 27.37; H, 3.59; N, 5.98. Found: C, 27.19; H, 3.43; N, 6.21.

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^{-1}. Elemental analyses of the compounds were obtained from a Thermoquest CE instrument (CHNS-O, Model EA/110).

Magnetic Measurements. Magnetic measurements were carried out with a Quantum Design MPMS 5S SQUID magnetometer in the temperature domain 2−300 K. The measurements were performed on crushed crystals from freshly isolated samples to avoid solvent loss. The powders were mixed with grease and put in gelatin capsules. The

Scheme 1. (a) Synthesis of the Homometallic Ln_4 Complexes by Using LH_3, Where both the Conformational Flexibility and Keto−Enol Tautomerism Were Utilized,[12] and (b) Synthesis of the Homometallic Ln_6 Complexes 1−4, Where Exclusively the Enol Form of LH_3 Is Present (This Work)



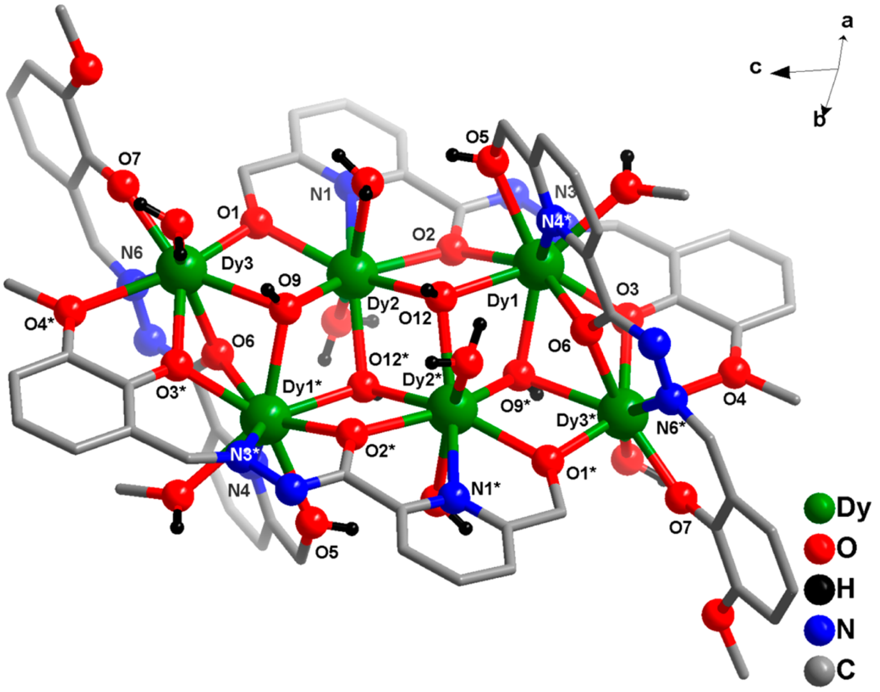


Figure 1. Tetracationic complex of 2. All hydrogen atoms have been removed, except those present in bridging hydroxide ligands or in coordinated solvent molecules. Chloride ions and solvent molecules of crystallization are not shown.

magnetic susceptibilities were measured in an applied field of 1000 Oe. The molar susceptibility (χ_M) was corrected for the sample holder and

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 2

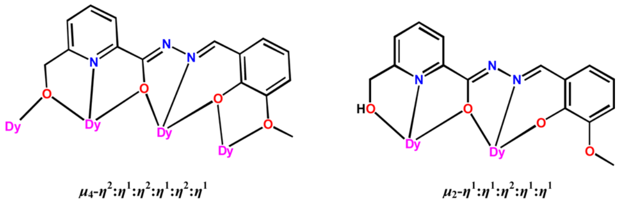
Bond Lengths			
Around Dysprosium(1)			
Dy(1)−O(2)	2.345(10)	Dy(1)−O(5)*[a]	2.440(13)
Dy(1)−O(3)	2.384(11)	Dy(1)−O(13)	2.475(10)
Dy(1)−O(9)*	2.399(11)	Dy(1)−N(3)	2.493(14)
Dy(1)−O(12)	2.422(9)	Dy(1)−N(4)	2.557(15)
Around Dysprosium(2)			
Dy(2)−O(9)	2.324(9)	Dy(2)−O(2)	2.403(10)
Dy(2)−O(1)	2.324(11)	Dy(2)−O(12)	2.443(10)
Dy(2)−O(12)*	2.398(10)	Dy(2)−N(1)	2.532(12)
Around Dysprosium(3)			
Dy(3)−O(7)	2.207(11)	Dy(3)−O(9)	2.453(11)
Dy(3)−O(1)	2.266(10)	Dy(3)−N(6)	2.529(12)
Dy(3)−O(6)	2.310(11)	Dy(3)−O(4)*	2.596(10)
Dy(3)−O(3)*	2.355(11)		
Bond Angles			
Dy(3)−O(1)−Dy(2)	110.1(4)	Dy(2)−O(9)−Dy(3)	103.9(4)
Dy(1)−O(2)−Dy(2)	114.0(4)	Dy(1)*−O(9)−Dy(3)	97.2(3)
Dy(3)*−O(3)−Dy(1)	100.3(4)	Dy(2)*−O(12)−Dy(1)	104.3(4)
Dy(3)−O(6)−Dy(1)*	103.4(4)	Dy(2)*−O(12)−Dy(2)	109.7(4)
Dy(2)−O(9)−Dy(1)*	107.4(4)	Dy(1)−O(12)−Dy(2)	109.9(4)

[a] Symmetry transformations used to generate equivalent atoms: (*) 1 − x + 1, −y + 1, −z + 1.

for the diamagnetic contribution of all atoms by using Pascal's tables. ac susceptibility was measured with an oscillating ac field of 3 Oe with frequency between 1 and 1500 Hz.

X-ray Crystallography. The crystal data for the compounds have been collected on a Bruker SMART CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å). The program SMART[15a] was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT[15a] for integration of the intensity of reflections and scaling, SADABS[15b] for absorption correction, and SHELXTL[15c,d] for space group and structure determination and least-squares refinements on F^2. All structures were solved by direct methods using the program SHELXS-97[15e] and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[15e] Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic figures have been generated using Diamond 3.1e software.[15f] The crystal data and cell parameters for compounds **1**−**4** are summarized in Table 1. The high residual density peaks in the range of 2.48−3.30 e Å^{-3} of all crystals are due to anomalous scattering of lanthanide ions, and the peaks are located very close to lanthanide centers (~1 Å). CCDC-977413 (**1**), CCDC-977414 (**2**), CCDC-977415 (**3**), and CCDC-977416 (**4**) contain crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Scheme 2. Binding Modes of the Ligands (L^{3-} and LH^{2-}) in 2


μ_4-η^2:η^1:η^2:η^1:η^2:η^1

μ_2-η^1:η^1:η^2:η^1:η^1

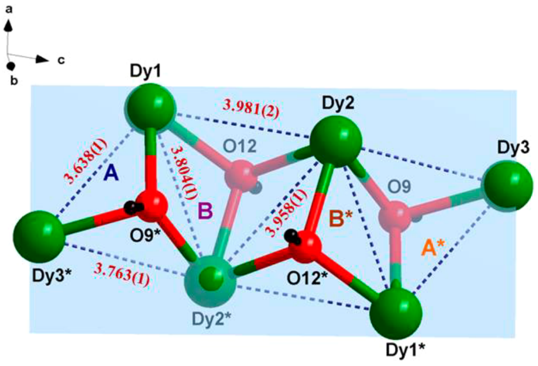


Figure 2. Hexanuclear core consisting of four fused triangular trimeric $[Dy_3(OH)]^{8+}$ subunits. Symmetry transformations used to generate equivalent atoms: (*) 1 − x + 1, −y + 1, −z + 1.

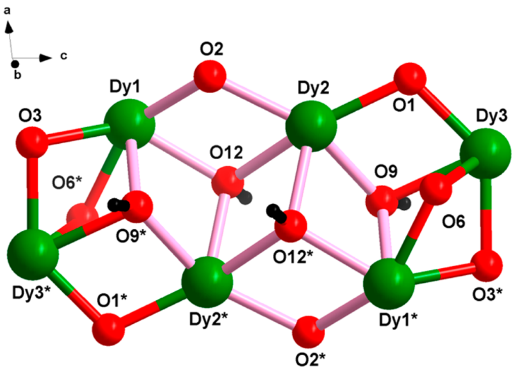


Figure 3. Dy_6 core present in **2**, highlighting (pink lines) an incomplete double-cubane Dy_4O_6 motif formed by face sharing. Symmetry transformations used to generate equivalent atoms: (*) 1 − x + 1, −y + 1, −z + 1.

■ RESULTS AND DISCUSSION

Synthetic Aspects. Multidentate Schiff base ligands,[11,16] particularly those derived from the condensation of *o*-vanillin and hydrazine units,[17,12] have been proven to be extremely effective for the preparation of homonuclear lanthanide complexes. We have recently prepared the ligand *N*′-(2-

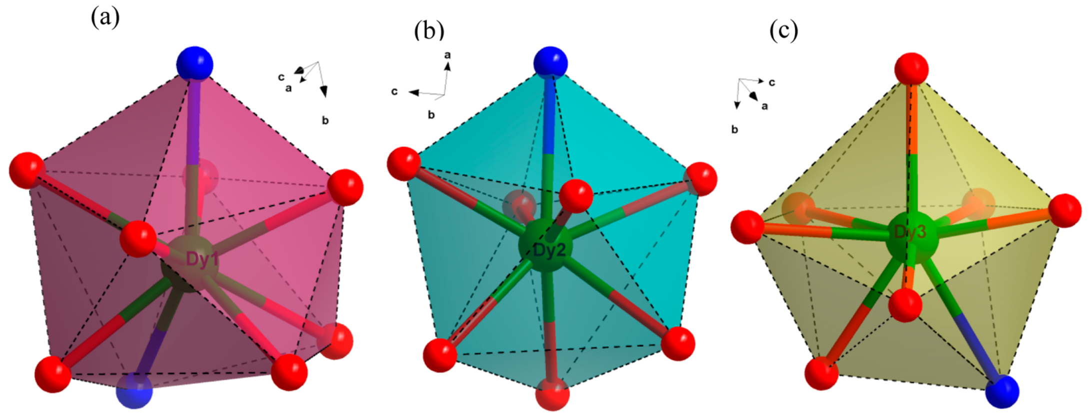


Figure 4. Different geometries around Dy(III) ions.

hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl)-picolinohydrazide (LH_3),[12] which allowed us to assemble tetranuclear compounds made up of two independent dimeric subunits (Scheme 1a).[12] In these complexes the pendant $-CH_2OH$ groups of the ligand were still not deprotonated. It was of interest to examine the effect of full deprotonation of the ligand LH_3 on the nuclearity of the ensemble. We were aware of the fact that the deprotonated $[-CH_2O]^-$ group would be able to participate in a bridging coordination mode and hence would facilitate the formation of a larger polynuclear complex. Accordingly, in the reaction of LH_3 with lanthanide metal salts in the presence of an excess of triethylamine (1:1.5:5), the hexanuclear complexes $[\{Ln_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_p[H_2O]_q[Cl]_4{\cdot}xH_2O{\cdot}yCH_3OH$ (**1**, Ln = Gd(III), $p = 4$, $q = 4$, $x = 8$, $y = 2$; **2**, Ln = Dy(III), $p = 2$, $q = 6$, $x = 8$, $y = 4$; **3**, Ln = Tb(III), $p = 2$, $q = 6$, $x = 10$, $y = 4$; **4**, Ln = Ho(III), $p = 2$, $q = 6$, $x = 10$, $y = 2$) (Scheme 1b) were formed.

This reaction is sensitive to the reaction conditions. Thus, in the presence of controlled amounts of base and pivalic acid as the coligand tetranuclear derivatives were obtained.[12] On the other hand, the use of only lanthanide nitrates as the precursors resulted in an insoluble precipitate in the presence of an excess of base. The reaction of lanthanide chlorides with LH_3 in the presence of an excess of base and pivalic acid afforded tetranuclear compounds in very low yields. Other products could not be isolated. Only under the reaction conditions shown in Scheme 1b could we isolate the hexanuclear compounds. The molecular structures of all four complexes (**1**−**4**) were determined by single-crystal X-ray crystallography (vide infra).

X-ray Crystallography. X-ray crystallographic analysis of **1**−**4** reveals that all of these complexes crystallize in the triclinic system in the centrosymmetric space group $P\bar{1}$ with $Z = 1$. All of these complexes are tetracationic and contain four chlorides as the counteranions. Compounds **1**−**4** possess nearly similar structural arrangements with only minor structural variations (Scheme 1b and the Supporting Information). We describe herein the molecular structure of **2** as a representative example. The molecular structure of **2** is given in Figure 1; those of **1**, **3**, and **4** are given in the Supporting Information (Figures S1−S3). Selected bond parameters of **2** are summarized in Table 2. Other bond parameters, including those of **1**, **3**, and **4**, are given in the Supporting Information (Tables S1−S3).

The molecular structure of **2** reveals that the six Dy(III) ions are tightly held together by two triply deprotonated L^{3-} ligands which are nonadentate (enolate form); each ligand holds together four different Dy^{III} ions (Dy3, Dy2, Dy1, and Dy3*) in a $\mu_4\text{-}\eta^2{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^2{:}\eta^1$ mode (Scheme 2). In this binding action the enolate form of the ligand is exclusively present. The hexanuclear ensemble thus formed is strengthened by the coordination action of four μ_3-OH groups (Figure 1). Finally, two $[LH]^{2-}$ ligands, still possessing intact $-CH_2OH$ groups, function in a hexadentate manner ($\mu_2\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^1{:}\eta^1$) holding two terminal lanthanide ions each (Dy3 and Dy1*) (Scheme 2). Thus, in the formation of **1**−**4**, the ligand functions exclusively in the enolate form, unlike in $[Ln_4(LH)_2(LH_2)_2(\mu_2\text{-}\eta^1\eta^1\text{-}Piv)_2(\eta^1\text{-}Piv)_4]{\cdot}2CHCl_3$[12] (Ln = Dy, Tb, Gd), where both the keto and enolate forms of the ligand are present (Scheme 1a).

Further analysis of the structure of **2** reveals some interesting features. Thus, **2** contains a hexanuclear $[Dy_6(OH)_4]^{14+}$ core consisting of triangular trimeric motifs $[Dy_3(OH)]^{8+}$ that are fused with each other (Figure 2); the μ_3-OH groups deviate from the lanthanide mean plane (Figure 2). The Dy- - -Dy distances found in the hexanuclear core are shown in Figure 2. The average Dy−O distance is 2.391 Å.

Considering the involvement of the enolate (μ_2; O2 and O2*) and μ_3-hydroxide ligands, the hexanuclear core shown in Figure 3 expands into a structure containing two face-sharing incomplete double cubes (Figure 3). Finally the structure is completed by the involvement of the other coordinating groups. An inspection of the metric parameters reveals that the average bond distances $Dy-\mu_3\text{-}O_{hydroxo}$ = 2.426 Å, $Dy-\mu_2\text{-}O_{Phenolate}$ = 2.359 Å, $Dy-\mu_2\text{-}O_{enolate}$ = 2.374 Å, and $Dy-\mu_2\text{-}O_{alkoxy}$ = 2.294 Å are similar to those found in the literature.[11,12,16g,19c,d]

Interestingly, in the formation of **2**, the two $[LH]^{2-}$ ligands lie approximately orthogonal to the Dy_6 mean plane. In contrast, the two $[L]^{3-}$ ligands are nearly in the same plane (Figure S4, Supporting Information).

The overall structure of **2** contains three structurally distinct Dy^{III} ions; two of these, Dy2 and Dy3, are eight-coordinate (7O, 1N), while the other, Dy1, is nine-coordinate (7O, 2N). The shapes of these coordination spheres have been evaluated by continuous shape measures analysis carried out with SHAPE.[18] The results (Figure 4 and Table S4 (Supporting Information)) reveal that Ln ions sit in environments that significantly deviate from an ideal geometry and cannot be described by a simple deformation of one of the possible geometries. The actual polyhedral shape for the eight-coordinated centers appears to be between a triangular dodecahedron and a biaugmented trigonal prism, while for

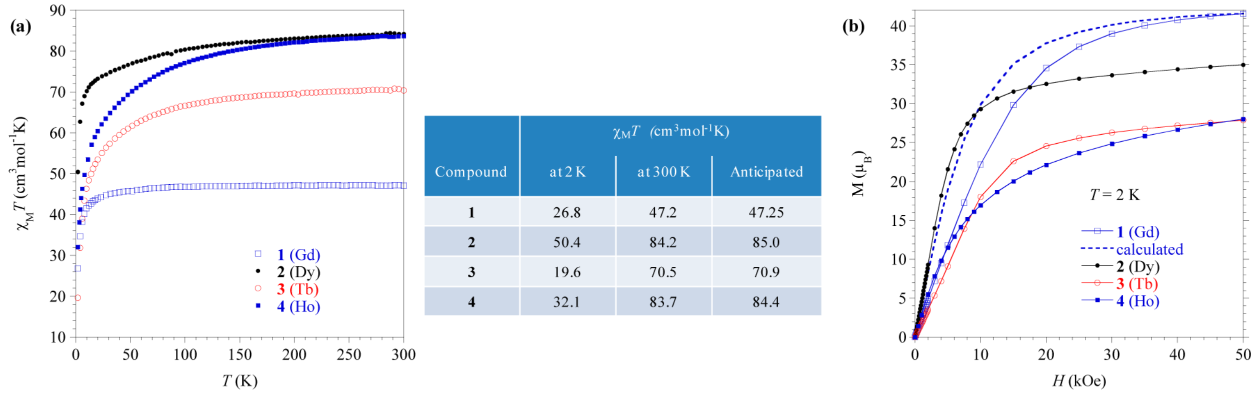
Table 3. Structural and Magnetic Features of Hexanuclear Lanthanide Asemblies

compound[a]	core topology	coordination no. (local geometry anound Ln(III) centers)	magnetic properties	ref
$[Dy_6(OAc)_3(\mu_3\text{-}CO_3)_2(L^1)_5(LH^1)(MeOH)_2]\cdot 4H_2O\cdot 5MeOH\cdot EtOH$	trigonal prism	8-coordinated (distorted-dodecahedral)	SMM; U_{eff} = 56 K, $\tau_0 = 6.6 \times 10^{-6}$ s	19a
$[Dy_6(apovh)_4(Hapovh)_4\ (CO_3)_2(SCN)_2]\cdot 6CH_3CN\cdot 8CH_3OH\cdot 2H_2O$	covalently linked pair of Dy_3 clusters	8- and 9-coordinated	SMM; U_{eff} = 29 K, $\tau_0 = 4.2 \times 10^{-6}$ s	19b
$[Dy_6L^2{}_4(\mu_4\text{-}O)(NO_3)_4(CH_3OH)]\cdot CH_3OH$	two Dy_3 triangles fused in an edge-to-edge manner	8-coordinated (distorted square antiprismatic), 9-coordinated (distorted monocapped square antiprismatic)	SMM; U_{eff} = 33.9, 40.7 K, $\tau_0 = 5.8 \times 10^{-8}$, 1.2×10^{-7} s	19c
$[Dy_6(\mu_3\text{-}OH)_3(\mu_3\text{-}CO_3)(\mu\text{-}OMe)(HL^3)_6(MeOH)_4(H_2O)_2]\cdot 3MeOH\cdot 2H_2O$	fusion of three O-capped triangular Dy_3 motifs which share vertices and edges	8-coordinated	SMM; U_{eff} = 5.6, 37.9 K, $\tau_0 = 4.2 \times 10^{-5}$, 3.8×10^{-6} s	19d
$[Dy_6(ovph)_4(Hpvph)_2Cl_4\ (H_2O)_2(CO_3)_2]\cdot CH_3OH\cdot H_2O\cdot CH_3CN$	triangular prism	8-coordinated (hula-hoop-like)	SMM; U_{eff} = 76 K, $\tau_0 = 1.2 \times 10^{-6}$ s	19e
$[Ln_6(teaH)_2(teaH_2)_2(CO_3)\ (NO_3)_2(chp)_7(H_2O)](NO_3)\cdot 4.5MeOH\cdot 1.5H_2O$ (Ln = Gd, Tb, Dy)	four coplanar Ln(III) ions in a trapezoid; two others lying above and below this plane	8-coordinated (distorted square antiprismatic) and 9-coordinated (distorted monocapped square antiprismatic)	SMM; Dy_6 analogue reveals out-of-phase ac susceptibility signals without showing peak maxima	19f
$[Dy_6(\mu_3\text{-}OH)_4L^4{}_4L^5{}_2\text{-}(H_2O)_9Cl][Cl]_5\cdot 15H_2O$	μ_3-OH-capped triangular units	8-coordinated	SMM; U_{eff} = 200 K, $\tau_0 = 1.5 \times 10^{-9}$ s	19g
$[Dy_6(\mu_3\text{-}OH)_4L^4{}_4(avn)_2\ (NO_3)_4(H_2O)_4](NO_3)_2\cdot H_2O\cdot 3(CH_3)_2CO$	μ_3-OH capped triangular units	8- and 9-coordinated	SMM; U_{eff} = 9.6 K, $\tau_0 = 2 \times 10^{-6}$ s	19h
$[Ln_6(teaH)_6(NO_3)_6]\cdot 8MeOH$ [Ln = Dy, Gd)	wheel	8-coordinated (distorted square antiprismatic)	out-of-phase ac susceptibility displays frequency dependence without resolving any peak maxima	19i
$[Dy_6(L^5)_4(\mu_3\text{-}OH)_4(CH_3OH)_2(NO_3)_2]\cdot 6CH_3CN$	edge-to-edge arrangement of two Dy_3 $(Dy_3(\mu_3\text{-}O)(\mu_3\text{-}OH))$ triangles	8-coordinated	SMM; U_{eff} = 3.2 K, $\tau_0 = 2.8 \times 10^{-5}$ s	19j
$[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(L^6)_4(H_2O)_{14}][Cl]_8\cdot 2L^6\cdot 6H_2O$ (Ln = Er, Ho, Dy) and $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8Cl_2(L^6)_4(H_2O)_{14}][Cl]_6\cdot 9H_2O$ (Ln = Gd, Tb)	octahedron	8-coordinated (distorted dodecahedral coordination) and 9-coordinated (monocapped square antiprismatic)	non-SMM	19k
$[Ln_6(L^7)_4(OH)_4(MeOH)_4][Cl]_2\cdot 4MeOH$ (Ln = Nd, Tb), $[Eu_6(L^8)_4(OH)_4(MeOH)_2(EtOH)_2(H_2O)_2][Cl]_2\cdot 3EtOH\cdot H_2O$, $[Er_6(L^8)_4(OH)_4(EtOH)_2(H_2O)_2][Cl]_2\cdot 2EtOH\cdot MeOH\cdot H_2O$	hexanuclear $[Dy_6(OH)_4]^{14+}$ core consisting of triangular trimeric motifs $[Dy_3(OH)]^{8+}$ fused to each other at the edge		magnetism not measd	19l
$[\{Ln_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_p[H_2O]_q[Cl]_4\cdot xH_2O\cdot yCH_3OH$ (**1**, Ln = Gd(III), $p = 4$, $q = 4$, $x = 8$, $y = 2$; **2**, Ln = Dy(III), $p = 2$, $q = 6$, $x = 8$, $y = 4$; **3**, Ln = Tb(III), $p = 2$, $q = 6$, $x = 10$, $y = 4$; **4**, Ln = Ho(III), $p = 2$, $q = 6$, $x = 10$, $y = 2$)	hexanuclear $[Dy_6(OH)_4]^{14+}$ core consisting of triangular trimeric motifs $[Dy_3(OH)]^{8+}$ fused to each other at the edge	8- and 9-coordinated (see Figure 3 and Table S4)	SMM; U_{eff} = 46.2 K, $\tau_0 = 2.85 \times 10^{-7}$ s (Dy analogue shows only SMM behavior)	this work

[a] Abbreviations: H_2L^1, (*E*)-*N*′-(2-hyborxy-3-methoxybenzylidene) pyrazine-2-carbohydrazide; H_2apovh, *N*′-(amino(pyridin-2-yl)methylene)-*o*-vanilloyl hydrazine; H_3L^2, formed by the in situ condensation of 2,6-diformyl-4-methylphenol and ethanolamine; H_2L^3, (*E*)-*N*′-(2-hydroxybenzylidene) pyrazine-2-carbohydrazide; H_2pvph, 3-methoxysalicylaldehyde picoloyl hydrazone; H_3tea, triethanolamine; Hchp, 6-chloro-2-hydroxypyridine; HL^4, *o*-vanillin; H_2L^5, 2-hydroxymethyl-6-methoxyphenol; H_2ava, 4-hydroxy-4-(2-hydroxy-3-methoxyphenyl)butan-2-one; H_3L^5, 1,3-bis(salicylideneamino)-2-propanol; L^6, 4-amino-3,5-dimethanyl-1,2,4-triazole; H_2L^7, *N*,*N*′-bis(3-methoxysalicylidene)(propylene-2-ol)-1,3-diamine; H_2L^8, *N*,*N*′-bis(salicylidene)(propylene-2-ol)-1,3-diamine.

Table 4. Comparison of the Average Bond Lengths (Å) and Bond Angles (deg) in the Hexanuclear Core Reported Here along with Those Belonging to Similar Cores Reported in the Literature

	Ln−-μ_3-O$_{\text{hydroxy}}$	Ln−μ_2-O$_{\text{phenolate}}$	Ln−N$_{\text{imine}}$	Ln−μ_3-O$_{\text{hydroxy}}$−Ln	ref
$[Ln_6(L^7)_4(OH)_4(MeOH)_4][Cl]_2\cdot 4MeOH$	2.442	2.341	2.542	95.4−110.1	19l
$[\{Ln_6(L)_2(LH)_2\}(\mu_3\text{-}OH)_4][MeOH]_p[H_2O]_q$; **1−4**	2.426	2.369	2.529	96.9−109.4	this work



Compound	$\chi_M T$ (cm^{3}mol^{-1}K) at 2 K	at 300 K	Anticipated
1	26.8	47.2	47.25
2	50.4	84.2	85.0
3	19.6	70.5	70.9
4	32.1	83.7	84.4

Figure 5. (a) Temperature dependence of $\chi_M T$ for **1**−**4** with detail of the $\chi_M T$ values found at the limits and the value anticipated at 300 K. (b) Field dependence of the magnetization obtained at 2 K (the solid lines are just guides for the eye). The dotted line corresponds to the calculated behavior for six noninteracting Gd(III) ions (see text).

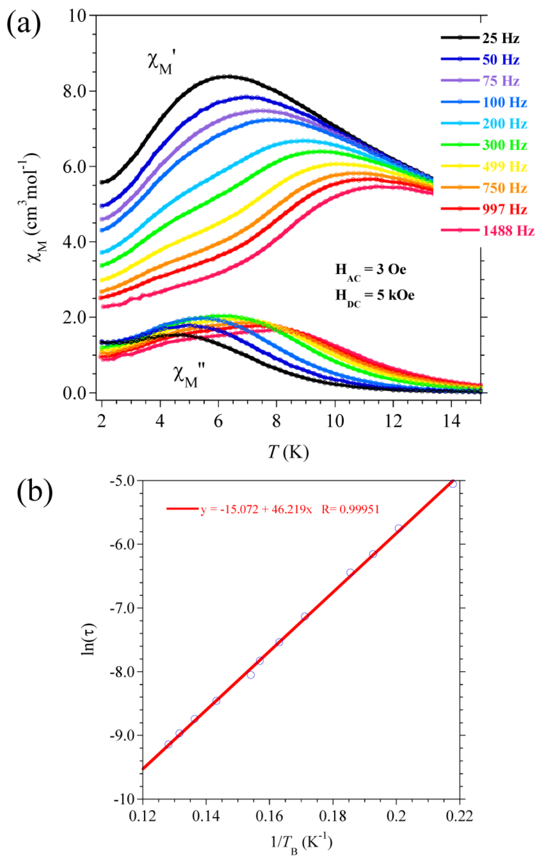


Figure 6. (a) Temperature dependence of χ_M' and χ_M'' ac susceptibility signals for **2** (measured with H_{ac} = 3 Oe and H_{dc} = 5 kOe). (b) Arrhenius plot and best fit (red line), yielding Δ/k_B = 46.2 K and $\tau_0 = 2.85 \times 10^{-7}$ s.

the nonacoordinated Ln spherical capped square antiprism, spherical tricapped trigonal prism, and muffin geometries delimitate the experimental shape.

It is interesting to compare the structural and magnetic features of the current family of Ln$_6$ complexes with those known in the literature (Table 3).[19] Generally, it is seen that most of the hexanuclear cores known in the literature involve *O-capped* triangular trimeric motifs which are fused to each other either at the vertices or at the edges. In addition, other topologies such as the wheel,[19i] the triangular prism,[19a,e] and the octahedron[19k] are also known. It is important to mention that, in spite of using a completely different ligand system, the core topology reported in this paper is similar to that reported by Jones et al.[19l] The latter did not perform magnetic measurements on their complexes. The metric parameters of the current Ln$_6$ family are very similar to those of other Ln$_6$ compounds that possess structurally similar cores (Table 4).

Magnetic Properties. The temperature dependence of $\chi_M T$ for **1**−**4** (χ_M stands for the molar magnetic susceptibility) is given in Figure 5. The $\chi_M T$ values obtained at 300 K are in agreement with the values anticipated for the six noninteracting Ln ions (see Figure 5 for details). For the four derivatives the value of $\chi_M T$ falls between 300 and 2 K with a faster drop at low temperature. While for **2**−**4** this decrease can be attributed to the crystal field effect,[20] the decrease observed for the Gd derivative **1** below 50 K reveals Gd−Gd exchange interactions. A fit of the Curie−Weiss law to the temperature dependence of $1/\chi_{Gd}$ (where χ_{Gd} is the magnetic susceptibility per Gd) yielded $\Theta = -1.5$ K and $C = 7.90$, thus confirming the occurrence of weak antiferromagnetic interactions. The field dependence of the magnetizations for **1**−**4** (Figure 5b) exhibit a fast increase for weak fields and a more gradual increase for stronger fields. For **1** the magnetization is compared to the behavior for six $S = {}^7/_2$ spins (with $g = 2$) in the absence of exchange interactions calculated by the Brillouin function[21] (dotted line in Figure 5b). It can be seen that the experimental curve runs below the calculated curve for any field below 45 kOe, which is further evidence for weak antiferromagnetic Gd−Gd interactions. For compounds **2**−**4** the magnetic anisotropy of the corresponding Ln ions also contributes to the gradual increase of M with the field.

The existence of SMM-type behavior for **2**−**4** was investigated by ac susceptibility measurements; only the Dy derivative exhibited evidence for slowly relaxing magnetization (Figure S5 (Supporting Information) for **3** and **4**). For **2** the out-of-phase susceptibility (χ_M'') is nonzero below 15 K but no well-defined peak is obtained in the absence of a static magnetic field, because of quantum tunneling of the magnetization (QTM) (Figure S6 (Supporting Information)). Applied dc fields allowed reducing the QTM components and led to rounded maxima for χ_M''. The behavior observed in the presence of a dc field of 5 kOe (Figure 6a and Figure S7 (Supporting Information)) revealed a frequency dependence of the in-phase (χ_M') and out-of-phase (χ_M'') ac signals. The blocking temperatures (defined as the peak of χ_M'' for a given frequency) is plotted in Figure 6b as ln τ versus $1/T_B$, where $\tau = 1/2\pi\nu$ is the corresponding relaxation time for a given frequency ν. The values obtained from a least-squares fitting of the Arrhenius law ($\tau = \tau_0 \exp\Delta/k_BT$) are $\Delta/k_B = 46.2$ K and $\tau_0 = 2.85 \times 10^{-7}$ s, confirming SMM-type behavior.

An evaluation of the distribution for the relation times from analysis of the Cole−Cole plot for **2** yielded a quite large α parameter (ca. 0.40; Figure S8 (Supporting Information)), which suggests a multipathway relaxation mechanism. This could be related to the structure of the compound that is made up by three different Dy(III) centers. All or at least two types of Dy could contribute to the observed overall slowly relaxing magnetization with slightly different characteristics, which hence lead to a distribution of relaxation times.

Now it has been well established that the magnetization blocking barrier (Δ/k_B) is highly susceptible to the coordination environments, ligand strength, and their positioning in the coordination sphere as well as the intercenter interactions.[22] The energy barrier for the magnetization reversal of $\Delta/k_B = 46.2$ K obtained here is moderately high and is in good agreement with the majority of hexanuclear Dy-based SMMs[19a,b,e] shown in Table 3. Table 3 also reveals that the higher energy barrier for magnetization reversal is associated mainly with the octacoordinated Dy(III) ions.

CONCLUSION

Ligand design and its utilization in the preparation of molecule-based magnets is an important subject. Subtle changes in the reaction conditions, even when the same ligand is employed, can lead to widely different results. This message is brought home very well in the current effort, which showed that the ligand *N*′-(2-hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl)picolinohydrazide (LH_3) can afford homonuclear [Ln_4][12] or [Ln_6] complexes under slightly different reaction conditions. The [$Ln]_6$ family described here possess a $[Ln_6(OH)_4]^{14+}$ core consisting of four fused $[Ln_3(OH)]^{8+}$ subunits. A detailed magnetic study of all complexes and particularly the gadolinium analogue revealed very weak antiferromagnetic interactions among the lanthanide ions. ac susceptibility measurements showed that only the dysprosium analogue is a SMM with the effective energy barrier $\Delta/k_B = 46.2$ K and relaxation time pre-exponential parameter $\tau_0 = 2.85 \times 10^{-7}$ s.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving molecular structures of **1**, **3**, and **4**, detailed structural parameters for compounds **1**, **3**, and **4**, magnetic data for **2**, and crystallographic data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data in CIF format for **1**−**4** have also been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 977413−977416. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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