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Octanuclear {Ln(III)$_8$}(Ln = Gd, Tb, Dy, Ho) Macrocyclic Complexes in a Cyclooctadiene-like Conformation: Manifestation of Slow Relaxation of Magnetization in the Dy(III) Derivative

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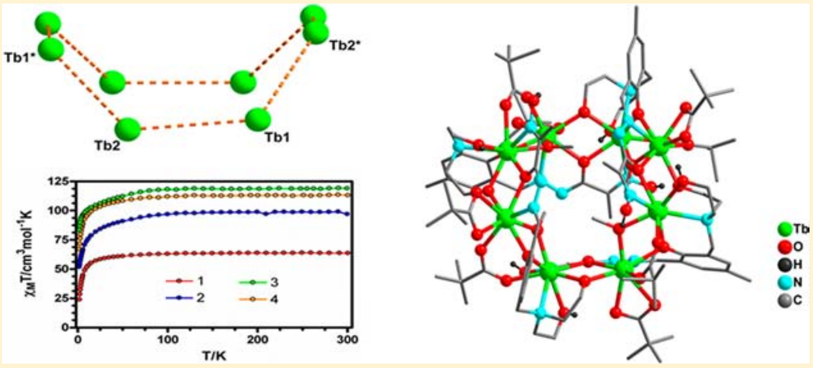
Supporting Information



ABSTRACT: The synthesis of a series of macrocyclic, isostructural octanuclear lanthanide complexes $[Gd_8\ (LH_2)_4\ (\mu\text{-Piv})_4\ (\eta^2\text{-Piv})_4\ (\mu\text{-OMe})_4]\cdot 6CH_3OH\cdot 2H_2O$ (**1**), $[Tb_8\ (LH_2)_4\ (\mu\text{-Piv})_4\ (\eta^2\text{-Piv})_4\ (\mu\text{-OMe})_4]_4CH_3OH\cdot 4H_2O$ (**2**), $[Dy_8(LH_2)_4\ (\mu\text{-Piv})_4\ (\eta^2\text{-Piv})_4\ (\mu\text{-OMe})_4]\cdot 8CH_3OH$ (**3**), and $[Ho_8(LH_2)_4(\mu\text{-Piv})_4\ (\eta^2\text{-Piv})_4\ (\mu\text{-OMe})_4]\cdot CH_3OH\cdot 4H_2O$ (**4**) have been achieved, using Ln(III) nitrate salts, pivalic acid, and a new multidentate chelating ligand (2*E*,*N*′*E*)-*N*′-(3-((bis(2- hydroxyethyl)amino)methyl)-2-hydroxy-5-methylbenzylidene)-2-(hydroxyimino) propane hydrazide (LH_5), containing two unsymmetrically disposed arms; one side of the phenol unit is decorated with a diethanolamine group while the other side is a hydrazone that has been built by the condensation reaction involving 2-hydroxyiminopropanehydrazide. All the compounds, **1**−**4**, are neutral and are held by the four $[LH_2]^{3-}$ triply deprotonated chelating ligands. In these complexes all the lanthanide ions are doubly or triply bridged via phenolate, alkoxy, and pivalate oxygens. The metal centers are distributed over the 8 vertices of an octagon, resembling a cyclooctadiene ring core. The details of magnetochemical analysis for complexes **1**−**4** shows that they exhibit antiferromagnetic interactions between the Ln^{3+} ions through the phenoxo, alkoxo, and pivalato bridging groups. None of the compounds exhibits slow relaxation of the magnetization at zero applied direct current (dc) magnetic field, which could be due to the existence of a fast quantum tunneling relaxation of the magnetization (QTM). In the case of **3**, the application of a small dc field is enough as to fully or partly suppress the fast and efficient zero-field QTM allowing the observation of slow relaxation above 2 K.

■ INTRODUCTION

For the past couple of years there has been notable interest in the preparation and structural elucidation of polynuclear lanthanide complexes.[1] This interest is the result of several factors. Many lanthanide(III) complexes are being investigated in view of their interesting catalytic,[2] photophysical[3] and magnetic properties.[4] Thus, lately, lanthanide compounds that function as single molecule magnets (SMMs),[5] single chain magnets,[6] and single ion magnets[7] have been studied. SMM behavior has been correlated to the presence of a large ground-state spin and a significant magnetic anisotropy within the molecule.[8] Since many lanthanide ions possess unquenched orbital angular momentum that result in magnetic anisotropy, along with a large number of unpaired 4f electrons, resulting in high spin, lanthanide complexes are being vigorously investigated as molecular magnetic materials.[9] Some envisaged applications of these novel magnetic materials include magnetic refrigeration,[10] ultra high-density data storage,[11] as well as quantum computation.[12] The first major breakthrough in this area was the discovery that the double-decker mononuclear sandwich-type lanthanide $[LnPc_2]$ (Ln = Tb (III), Dy(III),

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Ho(III) H_2Pc = phthalocyanine) complexes showed SMM behavior based on the single ion anisotropy of the constituent lanthanide ions.[13] Extending this idea, for the past couple of years, several multinuclear lanthanide aggregates have been reported, utilizing some multisite coordinating ligands.[5] Among these are the pentanuclear square-pyramid-shaped Dy(III) aggregate that showed the highest energy barrier (U_{eff} = 530 K) to magnetization reversal[14] and a $\{N_2\}^{3-}$ radical-bridged Tb(III) compound that showed a hysteresis up to 14 K.[15] In spite of these reports, polynuclear lanthanide complexes are still quite sparse. In this regard, from the point of view of chemical synthesis, there is a challenge to design appropriate ligands whose coordination action can lead to the generation of multinuclear lanthanide complexes. An examination of the literature revealed that the hydrazide-Schiff base ligands are very much useful for construction of lanthanide clusters.[5h,i,23,24c] Keeping this in mind we have designed a new chelating, flexible, and sterically unencumbered multisite coordinating ligand, (2*E*,*N*′*E*)-*N*′-(3-((bis(2-hydroxyethyl)-amino)methyl)-2-hydroxy-5-methylbenzylidene)-2-(hydroxy-imino) propane hydrazide (**LH$_5$**). Using this ligand, we have been able to assemble neutral octanuclear macrocyclic $\{$Ln(III)$\}_8$ complexes (Ln(III = Gd(III), Tb(III), Dy(III), and Ho(III)). These macrocycles possess a novel cyclooctadiene-type conformation. One of these, the Dy(III) analogue shows slow relaxation of magnetization above 2 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.[16] *p*-Cresol and paraformaldehyde were obtained from S.D. Fine Chemicals, Mumbai, India, and anhydrous magnesium chloride was obtained from Alfa Aesar and were used as such. $Ln(NO_3)_3\cdot nH_2O$ were obtained from Aldrich Chemical Co. and were used as such. 2-Hydroxy-5-methylbenzaldehyde (**C1**),[17] 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde (**C2**),[18] and (*E*)-2-(hydroxyimino)-propanehydrazide (**C4**)[19] were synthesized by adapting the literature procedure.

Syntheses. *3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylbenzaldehyde (**C3**).* 3-(Chloromethyl)-2-hydroxy-5-methylbenzaldehyde (**C2**) (6.00 g, 32.50 mmol) was taken in dry tetrahydrofuran (40 mL) and added dropwise to a mixture of diethanolamine (3.52 g, 33.50 mmol) and dry triethylamine (6.82 g, 67.50 mmol) taken in a solvent mixture of dry tetrahydrofuran (40 mL) and methanol (5 mL), under N_2 atmosphere. The reaction mixture was stirred at room temperature for 24 h. After this, the solution was filtered to remove triethylamine hydrochloride, and the filtrate was stripped off the solvent in vacuo to afford an oily mass. This was then dissolved in dichloromethane (40 mL) and washed twice with water (2 × 25 mL). The organic layer was separated, dried over anhydrous sodium sulfate, and the solvent from it in vacuo to afford an oily product. This was purified over a silica gel column (eluent: v/v: 5:95 methanol/ethyl acetate) to afford **C3** as a yellow liquid. Yield: 6.20 g, 75.3%. FT-IR (KBr) cm^{-1}: 3373 (b), 2870 (s), 1672(s), 1609 (s), 1473 (s) 1399 (m), 1278 (s), 1223 (s), 1150 (m), 1083 (s). ^1H NMR ($CDCl_3$, δ, ppm): 9.88 (s, 1H, −CHO), 7.26 (s, 1H, Ar−H), 7.18(s, 1H, Ar−H), 3.58 (t, 4H, CH_2O), 3.67 (s, 2H, $ArCH_2$), 2.63 (t, 4H, NCH_2), 2.24 (s, 3H, $ArCH_3$). ESI-MS (*m*/*z*): 254.139 (M+H). Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.37; H, 7.39; N, 5.37.

*(2E,N′E)-N′-(3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylbenzylidene)-2-(hydroxyimino)propanehydrazide (**LH$_5$**).* To a stirred solution of **C4** (2.54 g, 10.0 mmol) in dry methanol (20 mL), **C3** (1.18 g, 10.0 mmol) also dissolved in dry methanol (20 mL) was added dropwise over a period of 20 min, and the resulting reaction mixture was stirred for 12 h under N_2 atmosphere at 60 °C. The reaction mixture was allowed to come to room temperature and the solvent removed in vacuo affording a solid which was washed dichloromethane (3 × 10 mL) to give LH_5 as an off-white solid. Yield: 3.10 g, 87.8%. Mp: 122 °C. FT-IR (KBr) cm^{-1}: 3269 (b), 2920 (bm), 2826 (m), 1670 (s), 1613 (m) 1530 (s), 1470 (s) 1362 (s), 1234 (s), 1171 (s), 1034 (s), 958 (m). ^1H NMR (CD_3OD, δ, ppm): 8.48 (s, 1H, imino), 7.41 (s, 1H, Ar−H), 7.06(s, 1H, Ar−H), 3.79 (s, 2H, $ArCH_2$), 3.64 (t, 4H, CH_2O), 3.78 (s, 3H, OCH_3), 2.69 (t, 4H, NCH_2), 2.24 (s, 3H, $ArCH_3$), 2.03 (s, 3H, imino CH_3) ESI-MS (*m*/*z*): 353.176 (M+H). Anal. Calcd for $C_{16}H_{24}N_4O_5$: C, 54.53; H, 6.86; N, 15.90. Found: C, 54.40; H, 6.70; N, 15.73.

General Synthetic Procedure for the Preparation of the Complexes 1−4. All the metal complexes (**1**−**4**) were synthesized according to the following procedure. LH_5 (0.071 g, 0.20 mmol) was dissolved in methanol (10 mL) and subsequently $Ln(NO_3)_3\cdot nH_2O$ (0.40 mmol) was added to this solution. This reaction mixture was stirred for 0.5 h. At this stage, pivalic acid (0.041 g, 0.40 mmol) and triethylamine (0.1 mL, 0.70 mmol) were added, and the mixture was stirred for a further period of 4 h at room temperature affording a yellow precipitate. This was filtered, washed with cold methanol (2 × 5 mL), dried and dissolved in 1:1 v/v mixture of dichloromethane and methanol. X-ray quality crystals of **1**−**4** were obtained within a week after slow evaporation of the solvent mixture. The characterization data for these complexes are given below.

*$[Gd_8\ (LH_2)_4\ (\mu\text{-}Piv)_4\ (\eta^2\text{-}Piv)_4\ (\mu\text{-}OMe)_4]6CH_3OH\cdot 2H_2O$ (**1**).* Yield: 0.025 g, 26.2% (based on Gd). Mp: >220 °C. IR (KBr) cm^{-1}: 3362 (b), 2959 (s), 2925 (s), 2865 (m), 1621 (s), 1573 (s), 1541 (m) 1484 (s), 1420 (m), 1357 (s), 1305 (s), 1262 (s), 1223 (s), 1199 (s), 1135 (m), 1087 (s), 1046(s). ESI-MS *m*/*z*, ion: 1711.2, $[Gd_8\ (LH_2)_4\ (Piv)_6\ (OCH_3)_4\ (OH_2)_2]^{2+}$; 1683.1, $[Gd_8\ (LH_2)_4\ (Piv)_5\ (OCH_3)_5\ (HOCH_3)\ (OH_2)]^{2+}$. Anal. Calcd $C_{114}H_{198}N_{16}\ O_{48}Gd_8$ (3818.88): C, 35.85; H, 5.23; N, 5.87. Found: C, 35.38; H, 5.01; N, 5.75.

*$[Tb_8\ (LH_2)_4\ (\mu\text{-}Piv)_4\ (\eta^2\text{-}Piv)_4\ (\mu\text{-}OMe)_4]4CH_3OH\cdot 4H_2O$ (**2**).* Yield: 0.032 g, 33.3% (based on Tb). Mp: >220 °C. IR (KBr) cm^{-1}: 3341 (b), 2958 (s), 2901 (s), 2867 (m), 1622 (s), 1574 (s), 1543 (m) 1484 (s), 1421 (m), 1357 (s), 1303 (s), 1271 (s), 1222 (s), 1198 (s), 1135 (m), 1090 (s), 1046(s). ESI-MS *m*/*z*, ion: 1587.1, $[Tb_8\ (LH_2)_4\ (Piv)_3\ (OCH_3)_6\ (OH)]^{2+}$; 1615.1, $[Tb_8\ (LH_2)_4\ (Piv)_4\ (OCH_3)_4\ (OH)_2]^{2+}$ Anal. Calcd $C_{112}H_{192}N_{16}O_{48}Tb_8$ (3802.26): C, 35.38; H, 5.09; N, 5.89. Found: C, 35.10; H, 4.95; N, 5.75.

*$[Dy_8\ (LH_2)_4\ (\mu\text{-}Piv)_4\ (\eta^2\text{-}Piv)_4\ (\mu\text{-}OMe)_4]8CH_3OH$ (**3**).* Yield: 0.035 g, 36.1% (based on Dy). Mp: >220 °C. IR (KBr) cm^{-1}: 3349 (b), 2958 (s), 2902 (s), 2869 (m), 1622 (s), 1575 (s), 1546 (m) 1484 (s), 1421 (m), 1357 (s), 1304 (s), 1271 (s), 1222 (s), 1199 (s), 1135 (m), 1089 (s), 1048(s). ESI-MS *m*/*z*, ion: 1602.6, $[Dy_8\ (LH_2)_4\ (Piv)_3\ (OCH_3)_6\ (OH)]^{2+}$; 1574.1, $[Dy_8\ (LH_2)_4\ (Piv)_2\ (OCH_3)_8]^{2+}$. Anal. Calcd $C_{116}H_{200}\ N_{16}O_{48}\ Dy_8$ (3886.92): C, 35.84; H, 5.19; N, 5.77. Found: C, 35.50; H, 4.96; N, 5.60.

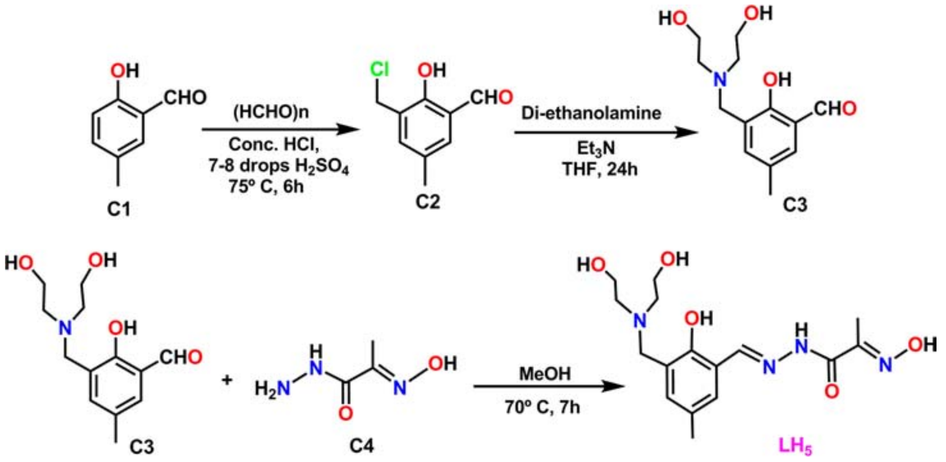
*$[Ho_8\ (LH_2)_4\ (\mu\text{-}Piv)_4\ (\eta^2\text{-}Piv)_4\ (\mu\text{-}OMe)_4]4CH_3OH\cdot 4H_2O$ (**4**).* Yield: 0.030 g, 31.2% (based on Ho). Mp: >220 °C. IR (KBr) cm^{-1}: 3345 (b), 2958 (s), 2903 (s), 2870 (m), 1624 (s), 1576 (s), 1547 (s) 1484 (s), 1421 (m), 1357 (s), 1304 (s), 1271 (s), 1222 (s), 1199 (s), 1135 (m), 1091 (s), 1048(s). ESI-MS *m*/*z*, ion: 1656.1, $[Ho_8(LH_2)_4(Piv)_4(OCH_3)_5(OH_2)(OH)]^{2+}$; 1684.7, $[Ho_8\ (LH_2)_4\ (Piv)_4(OCH_3)_4\ (OH_2)_5\ (OH)_2]^{2+}$. Anal. Calcd $C_{112}H_{192}\ N_{16}O_{48}Ho_8$ (3850.26): C, 34.94; H, 5.03; N, 5.82. Found: C, 34.58; H, 4.81; N, 5.61

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}. ^1H NMR was recorded on a JEOL-JNM LAMBDA model 400 spectrometer using $CDCl_3$ operating at 400 MHz. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. Electrospray ionization (positive ion, full scan mode) was used as was methanol as solvent for desolvation. Capillary voltage was maintained at 2 kV, and cone voltage was kept at 31 kV.

Table 1. Details of the Data Collection and Refinement Parameters for Compounds 1−4

	1	2	3	4
formula	$C_{114} H_{198} N_{16} O_{48} Gd_8$	$C_{112} H_{192} N_{16} O_{48} Tb_8$	$C_{116} H_{200} N_{16} O_{48} Dy_8$	$C_{112} H_{192} N_{16} O_{48} Ho_8$
M/g	3818.88	3802.26	3886.92	3850.26
crystal system	triclinic	tetragonal	tetragonal	tetragonal
space group	$P\bar{1}$	$I4(1)/a$	$I4(1)/a$	$I4(1)/a$
wavelength ($Mo_{K\alpha}$)	0.71069	0.71069	0.71069	0.71069
unit cell dimensions (Å, deg)	a = 17.936(5)	a = 18.261(3)	a = 18.228(3)	a = 18.183(3)
	b = 18.337(5)	b = 18.261(3)	b = 18.228(3)	b = 18.183(3)
	c = 26.005(5)	c = 44.911(9)	c = 44.831(9)	c = 44.626(9)
	α = 72.163(5)	α = 90	α = 90	α = 90
	β = 73.427(5)	β = 90	β = 90	β = 90
	γ = 65.490(5)	γ = 90	γ = 90	γ = 90
$V/Å^3$	7284(3)	14975(4)	14896(4)	14755(4)
Z	2	4	4	4
ρ_c/g cm^{-3}	1.741	1.686	1.733	1.730
μ/mm^{-1}	3.672	3.806	4.041	4.318
$F(000)$	3780	7520	7680	7584
cryst size (mm^3)	0.125 × 0.105 × 0.085	0.14 × 0.115 × 0.09	0.13 × 0.11 × 0.085	0.14 × 0.11 × 0.095
θ range (deg)	2.22 to 26.00°.	2.23 to 25.50	1.21 to 25.49	2.24 to 25.99
limiting indices	$-22 \leq h \leq 18$,	$-22 \leq h \leq 22$,	$-21 \leq h \leq 22$,	$-17 \leq h \leq 22$,
	$-22 \leq k \leq 22$,	$-22 \leq k \leq 22$,	$-22 \leq k \leq 21$,	$-22 \leq k \leq 22$,
	$-32 \leq l \leq 32$	$-38 \leq l \leq 54$	$-54 \leq l \leq 34$	$-50 \leq l \leq 54$
reflns collected	52005	40483	40419	41387
ind reflns	28460 [R(int) = 0.0333]	6960 [R(int) = 0.0549]	6918 [R(int) = 0.0907]	7223 [R(int) = 0.0592]
completeness to θ (%)	99.4	99.8	99.8	99.7
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	28460/56/1721	6960/15/433	6918/56/443	7231/42/409
goodness-of-fit on F^2	1.026	1.051	1.053	1.050
final R indices [$I > 2\sigma(I)$]	R1 = 0.0425,	R1 = 0.0475,	R1 = 0.0548,	R1 = 0.0492,
	wR2 = 0.0971	wR2 = 0.1242	wR2 = 0.1439	wR2 = 0.1222
R indices (all data)	R1 = 0.0607,	R1 = 0.0585,	R1 = 0.0820,	R1 = 0.0647,
	wR2 = 0.1065	wR2 = 0.1333	wR2 = 0.1685	wR2 = 0.1327
largest diff. peak and hole(e·Å^{-3})	3.175 and −1.224	2.595 and −1.257	2.467 and −1.674	2.211 and −1.456

Scheme 1. Synthesis of Ligand LH_5



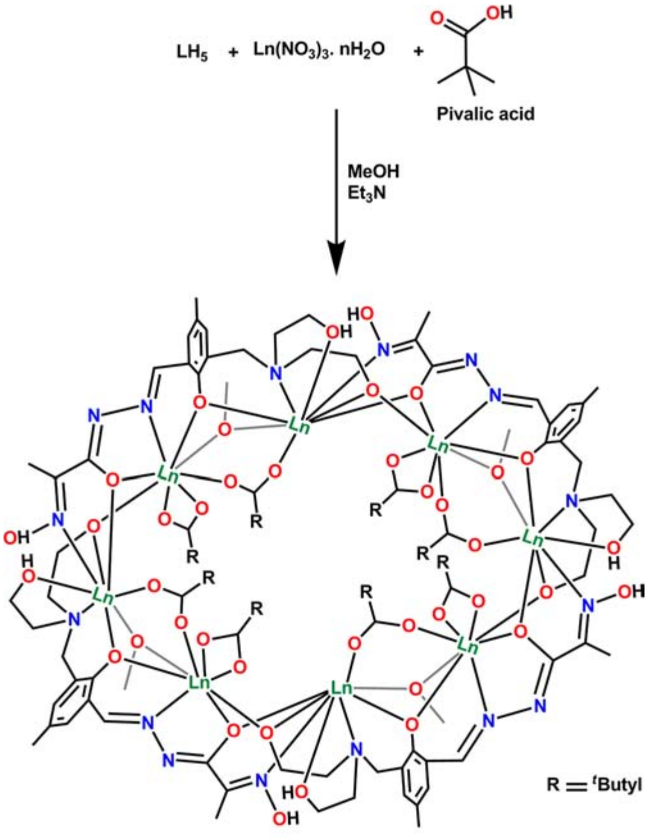
X-ray Crystallography. The crystal data and the cell parameters for **1**−**4** are given in Table 1. The crystal data for **1**−**4** have been collected on a Bruker SMART CCD diffractometer using a Mo Kα sealed tube. The program SMART[20a] was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT[20a] for integration of the intensity of reflections and scaling, SADABS[20b] for absorption correction, and SHELXTL[20c,d] for space group and structure determination and least-squares refinements on F^2. All the structures were solved by direct methods using the programs SHELXS-97[20e] and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[20e] 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 used in this manuscript have been generated using Diamond 3.1e software.[20f] In the case of **3** (Supporting Information, Figure S2), one carbon atom of the tertiary butyl group of chelating pivalic acid group is doubly disordered (C34A and C34B).

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 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.

■ RESULTS AND DISCUSSION

Synthetic Aspects. The multisite coordinating Schiff base ligand LH_5 was prepared by a three-step synthetic protocol involving the conversion of the precursor C1 to C3 and its subsequent condensation with C4 (Scheme 1). Thus, LH_5 is based on a basic phenol-framework and contains two unsymmetrically disposed arms; one side of the phenol unit is decorated with a diethanolamine group while the other side is a hydrazone that has been built by the condensation reaction involving 2-hydroxyiminopropanehydrazide (**C4**). Potentially LH_5 has 9 coordination sites although because of steric restrictions some of them would not be expected to participate in coordination. Further, the choice of the coordinating groups has been based on the literature precedent reports that they would favor binding to lanthanide ions. Thus, $-CH_2CH_2OH$ group from diethanolamine part has been shown in its both deprotonated and protonated forms to be effective for assembling 3d/4f and 4f compounds.[21] Similarly ligands built from vanillin and hydrazine-based motifs have found use in preparing mixed-valent manganese-containing polynuclear compounds.[22] Also, in situ generated ligands obtained by the condensation of hydrazine-based ligands with vanillin have been used to prepare 4f-containing compounds.[23] Another aspect that was considered in the design of LH_5 was that the ethanolamine side arm is sufficiently flexible and at the same time can provide a dual mode of binding. Thus, while the free form can function as a terminal ligand, the deprotonated form can act in a bridging mode. In accordance with all the above expectations, LH_5 reacts with $Ln(NO_3)_3 \cdot nH_2O$ and pivalic acid (PivH) (in a 1:2:2 stoichiometric ratio, in the presence of triethylamine as the base) in methanol affording the neutral macrocyclic octanuclear lanthanide(III) complexes, $[Ln_8(LH_2)_4(\mu\text{-Piv})_4(\eta^2\text{-Piv})_4(\mu\text{-OMe})_4]$ **1−4** in moderate yields (Scheme 2; see the experimental section for details of syntheses). The molecular structure of all the four complexes (**1−4**) was determined by single-crystal X-ray crystallography (vide infra). ESI-MS of **1−4** was carried out to check if the structural integrity of the macrocycles was maintained in solution. While the parent ion peaks could not be detected, we were able to find peaks that correspond to $[Gd_8(LH_2)_4(Piv)_5(OCH_3)_5(HOCH_3)(OH_2)]^{2+}$ (*m*/*e*: 1683.1), $[Gd_8(LH_2)_4(Piv)_6(OCH_3)_4(OH_2)_2]^{2+}$ (*m*/*e*: 1711.2); $[Tb_8(LH_2)_4(Piv)_3(OCH_3)_6(OH)]^{2+}$ (*m*/*e*: 1587.1), $[Tb_8(LH_2)_4(Piv)_4(OCH_3)_4(OH)_2]^{2+}$ (*m*/*e*: 1615.1); $[Dy_8(LH_2)_4(Piv)_2(OCH_3)_8]^{2+}$ (*m*/*e*: 1574.1), $[Dy_8(LH_2)_4(Piv)_3(OCH_3)_6(OH)]^{2+}$ (*m*/*e*: 1602.6); $[Ho_8(LH_2)_4(Piv)_4(OCH_3)_5(OH_2)(OH)]^{2+}$ (*m*/*e*: 1656.1), $[Ho_8(LH_2)_4(Piv)_4(OCH_3)_4(OH_2)_5(OH)_2]^{2+}$ (*m*/*e*: 1684.7) (see Figure 1 for a representative ESI-MS; see also Supporting Information).

Scheme 2. Synthesis of Compounds 1−4



Ln = Gd(**1**), Tb(**2**), Dy(**3**), Ho(**4**)

n = 5 (Dy, Tb); **n** = 6 (Gd, Ho).

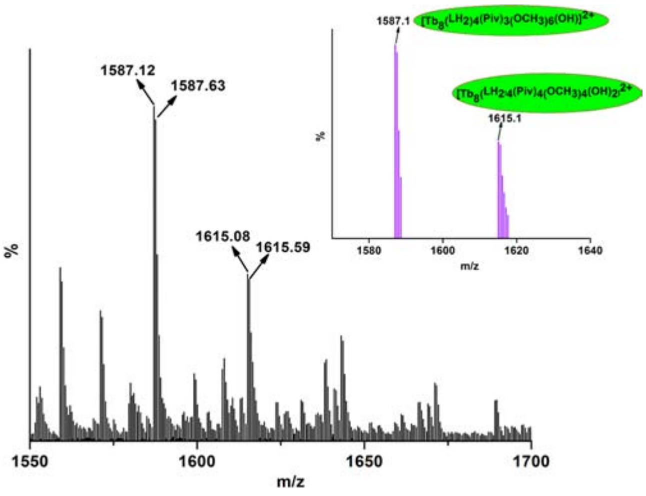


Figure 1. ESI-MS of **2** (inset picture shows isotopic distribution pattern of the two octanuclear fragments).

X-ray Crystallography. Single-crystal X-ray study revealed that the compounds **2−4** crystallize in the space group *I*4(1)/*a* whereas compound **1** crystallizes in triclinic space ($P\bar{1}$) group. The asymmetric unit of **2−4** contains one-fourth of the total molecule, namely, $[Ln_2(LH_2)(\mu\text{-Piv})(\eta^2\text{-Piv})(\mu\text{-OMe})]$ consisting of one triply deprotonated ligand $[LH_2]^{3-}$, two lanthanide ions, two pivalate ions, and one methoxide ion (Figure 3). On the other hand the asymmetric unit of **1** contains the full molecule. However, all of the compounds possess similar structural features. In view of this, in the following we describe the molecular structure of $[Tb_8(LH_2)_4(\mu\text{-Piv})_4(\eta^2\text{-Piv})_4(\mu\text{-OMe})_4]$ (**2**) as a representative example. The molecular structure of **2** is given in Figure 2. The structural details of all other compounds are given in the Supporting Information.

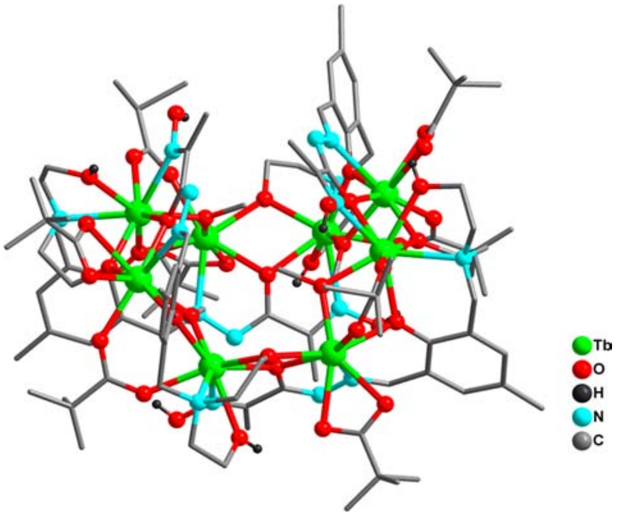


Figure 2. Molecular structure of **2** (hydrogen atoms and solvent molecules were omitted for clarity).

2 is a neutral 16-membered macrocycle (considering the shortest path involving Tb−O−Tb linkages) and possesses a wheel type structural topology (Figure 5). The macrocyclic core is made up of interconnected four-membered Tb_2O_2 rings with the terbium ions serving as the spirocyclic nodes. The assembly of the octanuclear macrocycle is made possible by the involvement of four triply deprotonated $[LH_2]^{3-}$ ligands which are arranged on the outer surface of the lanthanide wheel. This structural feature, presumably, is responsible for the favorable solubility of **2** in chlorinated organic solvents such as dichloromethane and chloroform. Among the 9 potential coordination sites on the ligand the hydrazine nitrogen (adjacent to the carbonyl carbon) and the hydroxylamine oxygen, do not participate in binding to the metal ions. Interestingly the C═O unit, presumably in its enolate form, functions as a bridging ligand binding two Tb(III) ions together. While one of the ethanolamine arms is deprotonated and acts as a briding ligand, the other, in its free form functions as part of chelating ligand along the nitrogen atom. Expectedly, the phenolate oxygen is involved in a bridging coordination mode. Both the imino nitrogen atoms are monodentate and form part of the chelating rings around the terbium ions (Scheme 2, Figure 3). Thus, overall, each LH_2^{3-} simultaneously binds to four terbium ions (Figure 4) in a μ_4- η^1: η^2: η^1: η^2: η^1: η^1: η^2 fashion. In addition to LH_2^{3-}, 8 pivalate ions are involved in coordination; four of these are chelating while four others are bridging. Finally, four methoxide ions are also involved in a bridging coordination. Thus, in the octanuclear core two adjacent Tb(III) ions such as Tb1 and Tb2 are bridged by the amido oxygen (O2) and one of the deprotonated ethanolic arms (O4); the immediate neighboring four-membered ring formed contains Tb1 and Tb2* that are bridged by the phenolate oxygen (O3) and the methoxide oxygen (O6). The inter-Tb(III) distance in the four-membered rings ranges from 3.855(4) Å and 3.733(4) with Tb−O−Tb angles of 104.2(2)−113.7(2)°. Overall, in the macrocycle, there are two types of Tb(III) ions. Both of these have a coordination number of 8; however, while Tb1 has a distorted square-antiprism geometry (7O, 1N), Tb2 has a distorted trigonal dodecahedral geometry

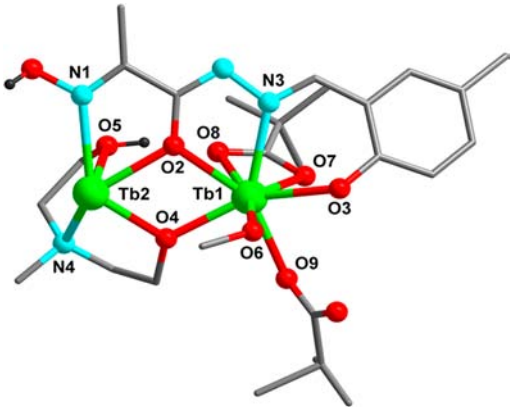


Figure 3. Asymmetric unit of **2** (hydrogen atoms and solvent molecules are omitted for clarity).

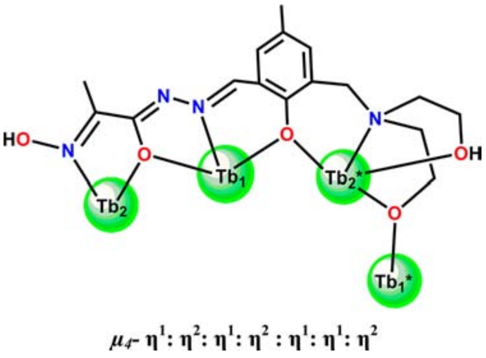


Figure 4. Binding mode of the ligand (**[LH$_2$]$^{3-}$**) with Terbium(III) ions.

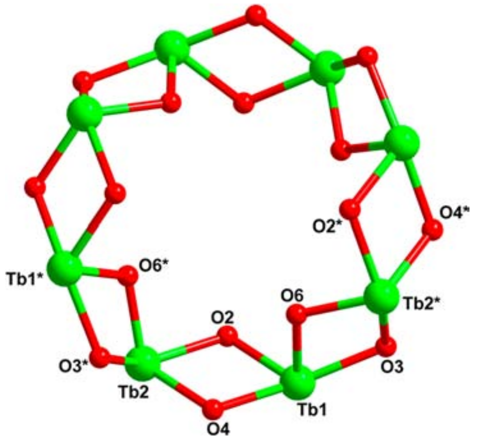


Figure 5. View of the of central Tb_8 core. Selected bond distances (Å) and bond angles (deg) are as follows Tb(1)−O(2) = 2.377(6), Tb(1)−O(4) = 2.312(6), Tb(1)−O(6) = 2.269(6), Tb(1)−O(3) = 2.369(6), Tb(2)−O(2) = 2.353(6), Tb(2)−O(4) = 2.292(6), Tb(2)−O(3)* = 2.361(6),Tb(2)−O(6)* = 2.266(6), Tb(1)−Tb(2) = 3.854 (8), Tb(2)−Tb(1)* = 3.733 (7). Tb(2)−O(2)−Tb(1) = 109.2(2), Tb(2)−O(4)−Tb(1) = 113.7(2), Tb(2)*−O(6)−Tb(1) = 110.8(2), Tb(2)*−O(3)−Tb(1) = 104.2(2), Tb(2)*−Tb(1)−Tb(2) = 121.54(2), Tb(1)*−Tb(2)−Tb(1) = 122.83 (2). * Atoms are generated by the symmetry operation −*y*+1/4, *x*+1/4, −*z*+1/4 and *y*−1/4, −*x*+1/4, −*z*+1/4.

(6O, 2N) (Figure 7). The Tb–O bond distances are nearly similar (average: 2.369 (6) Å) with the shortest distance of 2.269(6) Å being seen for the Tb–O bond involving the methoxide oxygen (Tb(1)–O(6)). In contrast, the longest distance, 2.528(7) Å involves the diethanolamine nitrogen (Tb(1)–N(3). The other Tb–O and Tb–N bond distances are unexceptional and are summarized in the caption of Figure 7.

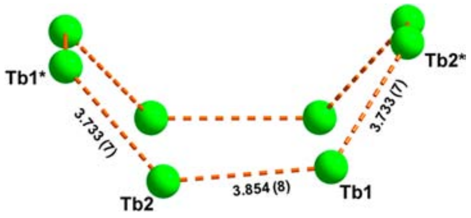


Figure 6. Arrangement of Tb_8 unit in cyclooctadiene-like conformation in **2**.

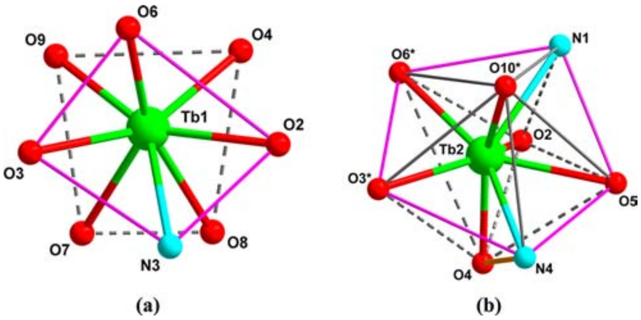


Figure 7. (a) Distorted square antiprism geometry around the Tb1 (b) Distorted trigonal-dodecahedron environment around the Tb2 ion in **2**. Selected bond distances (Å) are as follows Tb(1)–O(6) = 2.269(6), Tb(1)–O(4) = 2.312(6), Tb(1)–O(3) = 2.369(6), Tb(1)–O(9) = 2.369(6), Tb(1)–O(2) = 2.377(6), Tb(1)–O(7) = 2.459(7), Tb(1)–O(8) = 2.514(7), Tb(1)–N(3) = 2.528(7), Tb(2)–O(6)* = 2.266(6), Tb(2)–O(4) = 2.292(6), Tb(2)–O(2) = 2.353(6), Tb(2)–O(3)* = 2.361(6), Tb(2)–O(10)* = 2.394(6), Tb(2)–O(5) = 2.504(6), Tb(2)–N(1) = 2.542(7), Tb(2)–N(4) = 2.577(8).

Interestingly, all the 8 terbium ions present in the macrocycle are distributed over the 8 vertices of an octagon in a puckered configuration which resembles the cyclooctadiene ring core (Figure 6). The two planes, plane1(Tb1*, Tb2*, Tb1**, Tb2**) and plane2 (Tb1, Tb2, Tb1***, Tb2***) are almost parallel, and the mean plane deviation of the terbium atoms from the corresponding planes is given in the Supporting Information, Figure S4, Table S4–S5. Although some octanuclear lanthanide complexes are previously known (Table 2),[24] the current family has a different and unique topology.

The crystal structure of **2** reveals the presence of intermolecular C–H·····O interactions which assist in the formation of a supramolecular polymeric association along the crystallographic *a*-axis (Supporting Information).

Magnetic Properties. The temperature dependences of $\chi_M T$ for complexes **1**–**4** (χ_M is the molar magnetic susceptibility per Ln_8 unit) in the range 300–2 K were measured in an applied magnetic field of 0.1 T and are displayed in Figure 8. At room temperature, the $\chi_M T$ value for **1** (63.16 $cm^3\ mol^{-1}$ K) matches well with that expected for 8 noninteracting Gd^{3+} ions of 63 $cm^3\ mol^{-1}$ K (with $S = 7/2$, $g = 2.0$). On lowering the temperature, the $\chi_M T$ for **1** remains almost constant until ~50 K and then decreases sharply to reach a value of 23.8 $cm^3\ mol^{-1}$ K at 2 K. As the Gd^{3+} ions

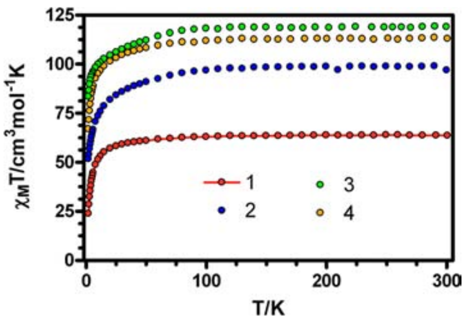


Figure 8. Temperature dependence of the $\chi_M T$ product for **1**–**4** . The red solid line shows the best fit for complex **1**.

Table 2. Structural and Magnetic Features of Octanuclear Lanthanide Asemblies

compound	core topology	magnetic property	ref.
$[Dy_8(\mu_4\text{-}CO_3)_4(L')_8\text{-}(H_2O)_8]\cdot 10MeOH\cdot 2H_2O$	tub-like conformation	SMM[b] $U_{eff} = 74.2$ K, $\tau_0 = 2.1 \times 10^{-6}$ s	5i
$[Dy_8(OH)_6(OMe)_6(cmnm)_{10}\ (ccnm)_2(H_2O)_2(MeOH)_2]\cdot 3H_2O\cdot 10MeOH$[a]	double cubane	SMM[c]	24a
$[Dy_8(\mu_3\text{-}OH)_4(ovn)_2(mvn)_2(p\text{-}NO_2bz)_{14}(CH_3OH)_2]\cdot 3.09CH_3CN\cdot 6CH_3OH\cdot 3H_2O$[a]	planar *S* shape	SMM[c]	24b
$[Dy_8(ovph)_8(CO_3)_4(H_2O)_8]\cdot 12CH_3CN\cdot 6H_2O$[a]	tub-like conformation	SMM[c]	24c
$[Gd_8(L'')_4(AcO)_8(EtOH)_4(H_2O)_4]\cdot 8EtOH\cdot 4H_2O$[a]	wheel-like core	non SMM[d]	24d
$Nd_8(L'')_4(AcO)_8(MeOH)_4(H_2O)_8]\cdot 4MeOH\cdot 24H_2O$[a]	wheel-like core	non SMM[d]	24d
$[Gd_8(LH_2)_4(\mu\text{-}Piv)_4(\eta^2\text{-}Piv)_4(\mu\text{-}OMe)_4]\cdot 6CH_3OH\cdot 2H_2O$	cyclooctadiene conformation	non SMM[d]	this work
$[Tb_8(LH_2)_4(\mu\text{-}Piv)_4(\eta^2\text{-}Piv)_4(\mu\text{-}OMe)_4]\cdot 4CH_3OH\cdot 4H_2O$	cyclooctadiene conformation	non SMM[d]	this work
$[Dy_8(LH_2)_4(\mu\text{-}Piv)_4(\eta^2\text{-}Piv)_4(\mu\text{-}OMe)_4]\cdot 8CH_3OH$	cyclooctadiene conformation	SMM[c]	this work
$[Ho_8(LH_2)_4(\mu\text{-}Piv)_4(\eta^2\text{-}Piv)_4(\mu\text{-}OMe)_4]\cdot 4CH_3OH\cdot 4H_2O$	cyclooctadiene conformation	non SMM[d]	this work

[a] Abbreviations: H_2L' = (*E*)-*N*′-(2-hyborxy-3-methoxybenzylidene)pyrazine-2-carbohydrazide; cmnm = cyano(imino(methoxy)methyl)nitrosomethanide; ccnm = carbamoyl-cyano nitrosomethanide; ovnH = *o*-vanillin; $mvnH_2$ = methyl hemiacetal derivative of *o*-vanillin; $p\text{-}NO_2bz$ = *p*-nitrobenzoate; H_2ovph = *o*-vanillin picolinoylhydrazone; H_4L'' = sulfonylcalix[4]arene. [b] Ferromagnetic ground state. [c] Antiferromagnetic ground state; absence of maxima in the frequency dependent χ_M'' vs *T* plot. [d] Antiferromagnetic ground state.

present no spin−orbit coupling at the first order, the decrease of the $\chi_M T$ at low temperature points directly to the presence of a very weak antiferromagnetic interaction between the Gd^{3+} ions of the wheel-shaped octanuclear Gd_8 complex and/or zero-field splitting (ZFS) effects of the Gd^{3+} ions. The field dependence of the magnetization at 2 K for **1** (Figure 9) shows a sigmoidal shape at low field, which supports the antiferromagnetic interaction and/or ZFS in this complex. As expected, the experimental magnetization values are well below the Brillouin function for 8 noninteracting Gd^{3+}ions. At high field the saturation of the magnetization is almost complete at 5 T, reaching a value of 55.35 NμB, which agrees well with the theoretical saturation value for 8 Gd^{3+} ions of 56 NμB.

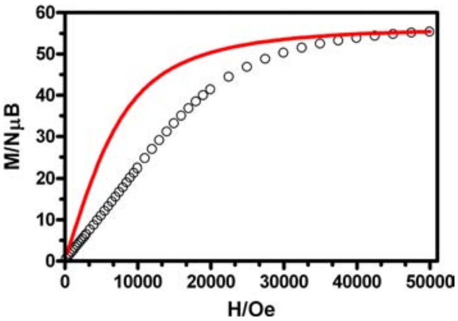


Figure 9. *M* vs *H* plots for **1** at 2 K. The red solid line represents the Brillouin function for 8 noninteracting Gd^{3+} ions.

The magnitude of the antiferromagnetic exchange interaction in **1** could not be determined by diagonalization matrix methods because the extremely high dimension of the matrices to be diagonalized for a Gd_8 system. It should be noted that there are two different types of bridging units in **1** with double dialkoxo and triple alkoxo/phenoxo/pivalate bridging groups. As previously pointed by some authors for diphenoxo-bridged Gd_2 complexes,[25] it seems that *J* becomes more negative as the Gd−O−Gd, and consequently the Gd···Gd, decrease. In view of this, the larger magnetic coupling (*J*) would take place between the Gd^{3+} ions connected by a triple bridge (short Gd···Gd distance), whereas the smaller magnetic coupling (*J*′) would be assigned to the dialkoxo-bridging pathway (long Gd···Gd distance). To estimate the value of the magnetic exchange coupling in **1** we have used a very crude model, in which each wheel has been considered to be formed by 4 equal dinuclear Gd_2 units with an intradinuclear magnetic interaction characterized by the *J* parameter and interdinuclear interactions that can be calculated by using the molecular field theory. Taking into account the above considerations, the experimental data were analyzed with the following Hamiltonian:

$$\mathbf{H} = -JS_{\mathrm{Gd1}}S_{\mathrm{Gd2}} - zJ'\langle S_z\rangle \mathbf{S_z}$$

The best fitting parameters were $J = -0.19$ cm^{-1}, $zJ' = -0.1$, and $g = 2.018$ with $R = 1.2 \times 10^{-7}$. Although the obtained values are in good agreement with the reported coupling constants for phenoxo-bridged Gd^{III} system complexes, with or without additional carboxylate bridging groups,[25,26] they should be taken with caution because of (i) the crudeness of the model, (ii) *J* and *J*′ are correlated, (iii) the possible existence of ZFS splitting of the Gd^{3+} ions.

The room temperature $\chi_M T$ values of complexes **2**−**4** are 96.9, 118.9, and 113 cm^3 mol^{-1} K, respectively, which are in rather good agreement with the expected theoretical values using the free ion approximation (94.6, 113.4, and 112.6 cm^3 mol^{-1} K for **2**, **3**, and **4**, respectively) for 8 noninteracting lanthanide ions: Tb^{3+}($^7F_6$, $S = 3$, $L = 3$, $g = 3/2$, $C = 11.82$ cm^3 mol^{-1} K), Dy^{3+} ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.$ cm^3 mol^{-1} K), and Ho^{3+} ($^5I_8$, $S = 2$, $L = 6$, $g = 5/4$, $C = 14.08$ cm^3 mol^{-1} K). The $\chi_M T$ product decreases with decreasing temperature, first slowly down to 100 K and then rapidly to 51.7, 83.5, and 67.0 cm^3 mol^{-1} K at 2.0 K for **2**−**4**, respectively. The decrease observed in the $\chi_M T$ values is most likely due to a combination of some very weak $Ln^{3+}\cdots Ln^{3+}$ antiferromagnetic interactions and possibly other effects such as magnetic anisotropy/ligand field and thermal depopulation of the Stark sublevels of the $^{2S+1}\Gamma_J$ ground state of the Ln^{3+} ion. The existence of very weak antiferromagnetic interactions in complexes **2**−**4** is not unexpected in view of the fact that isostructural Gd^{3+}, Tb^{3+}, Dy^{3+}, and Ho^{3+} complexes generally display magnetic exchange interactions of the same nature.[27] The magnetic data on these Ln^{3+} systems clearly show a nonzero spin ground state presumably originated from the closely spaced M_J Stark sublevels.[28]

The field dependence of the magnetization at 2 K for compounds **2**−**4** (Figure 10) shows a slow increase of the magnetization at low field and a linear increase at high field without achieving a complete saturation at 5 T. This behavior suggests the presence of a significant magnetic anisotropy and/or more likely the presence of low-lying excited states that are partially [thermally and field-induced] populated. These low-lying excited states are in agreement with weak magnetic interactions expected for 4f-4f systems. The magnetization values for **2**−**4** at 5 T (40.1, 46, 49.29 NμB, respectively) are considerably smaller than the expected saturation magnetization value, $M_s/N\mu_B = 8g_J J$, for 8 Ln^{3+} ions. The observed values at 5 T per Ln^{3+} ion are similar those estimated and observed for mononuclear Ln^{3+} complexes where the ligand-field effects eliminates the *J*-fold degeneracy of the $^{2S+1}\Gamma_J$ ground state.[28b,29]

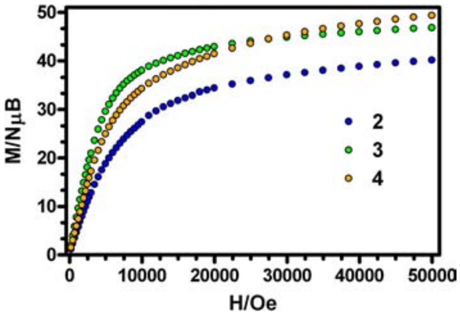


Figure 10. Field dependence of the magnetization for compounds **2**−**4**.

Dynamic ac magnetic susceptibility measurements as a function of the temperature at different frequencies were performed on complexes **2**−**4** under zero-external field but none of them showed a frequency dependency of the in-phase (χ'_M) and out-of-phase (χ''_M) signals. This behavior could be due to the existence of a fast quantum tunneling relaxation of the magnetization (QTM) promoted by intermolecular dipolar interactions and/or hyperfine interactions. When the ac measurements were performed in the presence of a small external dc field of 1000 Oe, to fully or partly suppress the possible fast quantum tunneling relaxation, only compound **3** showed slow relaxation of the magnetization but without exhibiting any maximum in the temperature dependence of χ''_M above 2 K at frequencies reaching 1400 Hz (see Supporting Information, Figure S10). This behavior suggests that **3** may exhibit SMM behavior below 2 K.

■ CONCLUSION

In summary, we have synthesized a series of macrocyclic, isostructural, neutral octanuclear lanthanide complexes; the $\{Ln(III)_8\}$ core has a cyclooctadiene-like conformation. Overall, the macrocycle contains two types of lanthanides, both with a coordination number of 8; while the geometry around one of these is distorted square pyramidal, the other is distorted trigonal dodecahedron. Compounds **1**−**4** exhibit antiferromagnetic interactions between the Ln^{3+} ions through the phenoxo, alkoxo, and pivalato bridging groups. None of these compounds exhibits slow relaxation of the magnetization at zero applied dc magnetic field which is due to the existence of a fast QTM. However, in the case of **3**, the application of a small dc field is enough so as to fully or partly suppress the fast and efficient zero-field quantum tunneling of magnetization allowing the observation of slow relaxation above 2 K.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. Further details are given in Figures S1−S10 and Tables S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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