Rhombus-Shaped Tetranuclear [Ln₄] Complexes [Ln = Dy(III) and Ho(III)]: Synthesis, Structure, and SMM Behavior

Vadapalli Chandrasekhar,*,[†,‡] Sakiat Hossain,[†] Sourav Das,[†] Sourav Biswas,[†] and Jean-Pascal Sutter*,[§,∥]

[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India

[‡]Tata Institute of Fundamental Research, Centre for Interdisciplinary Sciences, 21 Brundavan Colony, Narsingi, Hyderabad-500075, India

[§]CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, F-31077 Toulouse, France

[∥]Université de Toulouse, UPS, INPT, LCC, F-31077 Toulouse, France

S *Supporting Information*

ABSTRACT: The reaction of a new hexadentate Schiff base hydrazide ligand (LH_3) with rare earth(III) chloride salts in the presence of triethylamine as the base afforded two planar tetranuclear neutral complexes: $[\{(LH)_2Dy_4\}(\mu_2\text{-}O)_4]\cdot(H_2O)_8\cdot2CH_3OH\cdot8H_2O$ (**1**) and $[\{(LH)_2Ho_4\}(\mu_2\text{-}O)_4]\cdot(H_2O)_8\cdot6CH_3OH\cdot4H_2O$ (**2**). These neutral complexes possess a structure in which all of the lanthanide ions and the donor atoms of the ligand remain in a perfect plane. Each doubly deprotonated ligand holds two Ln(III) ions in its two distinct chelating coordination pockets to form $[LH(Ln)_2]^{4+}$ units. Two such units are connected by four $[\mu_2\text{-}O]^{2-}$ ligands to form a planar tetranuclear assembly with an Ln(III)₄ core that possesses a rhombus-shaped structure. Detailed static and dynamic magnetic analysis of **1** and **2** revealed single-molecule magnet (SMM) behavior for complex **1**. A peculiar feature of the χ_M'' versus temperature curve is that two peaks that are frequency-dependent are revealed, indicating the occurrence of two relaxation processes that lead to two energy barriers (16.8 and 54.2 K) and time constants ($\tau_0 = 1.4 \times 10^{-6}$ s, $\tau_0 = 7.2 \times 10^{-7}$ s). This was related to the presence of two distinct geometrical sites for Dy(III) in complex **1**.
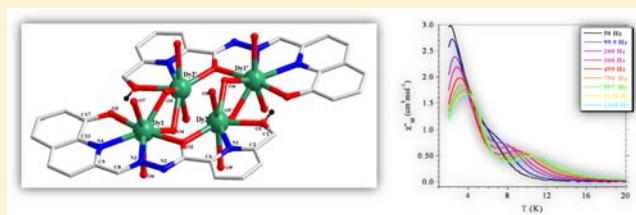
INTRODUCTION

There has been vigorous research activity in recent years in several laboratories around the world in the area of molecule-based magnetic materials such as single-molecule and single-chain magnets (SMMs and SCMs).[1] This interest stems from several points of view. The first aspect of interest is the exciting potential of these new materials for use in exotic applications, including data storage through quantum computation and spintronics,[2] and magnetic refrigeration.[3] In this regard, the deposition of SMMs on surfaces and their utilization in devices are emerging areas of interest.[2b,4] The second aspect of interest in molecule-based magnetic materials is that these systems offer the opportunity to study and to understand exotic physical phenomenon such as quantum tunneling of the magnetization,[5] finite size effects,[1k,6] quantum phase interference,[7] quantum super positions,[8] magnetic deflagration,[9] and so forth. The third point of interest, which is in the exclusive domain of chemists, is to devise reliable synthesis strategies that allow the assembly of multitudes of families of these new exotic materials. Accordingly, several polynuclear transition metal ions,[10] mixed transition−lanthanide metal ions (3d−4f),[11] and homometallic lanthanide ion aggregates[12] have been prepared and studied, and some of them have been shown to be SMMs. In this series, compounds containing lanthanide ions, such as Dy(III), Tb(III), and Ho(III), are of interest because they

possess relatively high spins (Dy(III) = $^{15}/_2$, Tb(III) = 6, Ho(III) = 8) and an intrinsic magnetic anisotropy. The latter is the result of the splitting of the spectroscopic ground level by a crystal field.[13] In this context, Ishikawa's double-decker complex, $[Pc_2Tb]^-$, remains a spectacular example with a high blocking temperature.[14] Among the homometallic lanthanide ion-containing systems, those containing Dy(III) have received considerable attention, and complexes with a nuclearity that varies from 1 to 11 [Dy₁,[15] Dy₂,[16] Dy₃,[17] Dy₄[12b,18] Dy₅,[19] Dy₆,[20] Dy₇,[21] Dy₈,[22] Dy₉,[23] Dy₁₀,[24] Dy₁₁[25]] are known in the literature. Some of these compounds have been shown to exhibit SMM behavior. We have been involved in designing ligands, such as SP[N(Me)N=CH−C₆H₃−2−OH−3−OMe]₃, that allow the assembly of heterometallic trinuclear 3d−4f compounds. Using a related ligand system[{NC(N-(CH₃)₂)}₂{NP{N(CH₃)N=CH−C₆H₃-(*o*-OH)(*m*-OCH₃)}₂}] and [{N₂P₂(O₂C₁₂H₈)₂}{NP{N(CH₃)N=CH−C₆H₃(*o*-OH)(*m*-OCH₃)}₂}] we could prepare heterometallic dinuclear 3d−4f compounds.[26] However, it was not possible to access homometallic lanthanide(III) assemblies using either of these ligands, and it was clear that a multi-site-coordinating, multi-compartmental ligand was required. Compartmental

Table 1. Details of the Data Collection and Refinement Parameters for Complexes 1 and 2

formula	$C_{36}H_{64}Dy_4N_8O_{28}$	$C_{40}H_{72}Ho_4N_8O_{28}$
M/g	1706.93	1772.76
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimensions (Å, deg)	$a = 10.552(5)$	$a = 10.431(4)$
	$b = 11.547(5)$	$b = 11.430(4)$
	$c = 11.927(5)$	$c = 11.838(4)$
	$\alpha = 104.585(5)$	$\alpha = 105.040(6)$
	$\beta = 91.465(5)$	$\beta = 91.041(7)$
	$\gamma = 104.431(5)$	$\gamma = 104.007(7)$
$V/Å^3$	1356.0(10)	1317.6(8)
Z	1	1
$\rho_c/g\ cm^{-3}$	2.090	2.186
μ/mm^{-1}	5.540	6.037
$F(000)$	812	822
cryst size (mm^3)	$0.05 \times 0.03 \times 0.02$	$0.15 \times 0.12 \times 0.10$
θ range (deg)	2.00 to 25.50	1.79 to 25.50
limiting indices	$-12 \leq h \leq 12$	$-12 \leq h \leq 7$
	$-11 \leq k \leq 13$	$-13 \leq k \leq 13$
	$-14 \leq l \leq 14$	$-14 \leq l \leq 14$
reflns collected	7296	7042
independent reflns	4945 [R(int) = 0.0247]	4809 [R(int) = 0.0482]
completeness to θ (%)	97.9%	97.9%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	4945/14/360	4809/114/351
goodness of fit on F^2	1.062	1.052
final R indices $[I > 2\theta(I)]$	R1 = 0.0703, wR2 = 0.2011	R1 = 0.0855, wR2 = 0.2179
R indices (all data)	R1 = 0.0863, wR2 = 0.2365	R1 = 0.1299, wR2 = 0.2797
largest diff. peak and hole (e $Å^{-3}$)	3.858 and −2.766	3.733 and −3.028 e·$Å^{-3}$

Schiff base ligands have been used in the preparation of polynuclear lanthanide-containing compounds.[17b,18c,27] In the current study, our ligand design retained the hydrazine part of the aforementioned phosphorus-supported ligands but varied the remaining portion. Accordingly, we assembled (6-hydroxymethyl)-N'-((8-hydroxyquinolin-2-yl)methylene)-picolinohydrazide(LH_3), and we used this to construct neutral homotetranuclear Dy_4 and Ho_4 assemblies $[\{(LH)_2Dy_4\}(\mu_2\text{-}O)_4](H_2O)_8\cdot2CH_3OH\cdot8H_2O$ (**1**) and $[\{(LH)_2Ho_4\}(\mu_2\text{-}O)_4]\cdot(H_2O)_8\cdot6CH_3OH\cdot4H_2O$ (**2**). Magnetic measurements on **1** were carried out and revealed it to be an SMM. These results are discussed in this Article.

■ EXPERIMENTAL SECTION

Reagents and General Procedures. The common reagents and the solvents that were used in this work were purified according to standard procedures.[28a,b] Methyl-6-(hydroxymethyl)picolinate[28c] and 8-hydroxy-2-quinolinecarboxaldehyde[29] were prepared by adapting procedures that have been reported. Pyridine-2,6-dicarboxylic acid, $NaBH_4$, SeO_2, 2-methyl-8-quinolinol, $DyCl_3\cdot6H_2O$, and $HoCl_3\cdot6H_2O$ (Sigma Aldrich) were used as received. Hydrazine hydrate was obtained from Merck and was used as received.

Instrumentation. Melting points were measured using a JSGW apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instrument model EA/110 CHNS-O elemental analyzer. ^1H NMR was recorded on a JEOL-JNM LAMBDA 400 model NMR spectrometer in a $CDCl_3$ solution. The chemical shifts are referenced with respect to $SiMe_4$. IR spectra were recorded in KBr pellets on a Bruker Vector 22 FT IR spectrophotometer that was operating from 400 to 4000 cm^{-1}.

Magnetic measurements were carried out with a Quantum design MPMS 5S SQUID susceptometer in the temperature range from 2 to 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 magnetic susceptibilities were measured in an applied field of 1000 Oe. The molar susceptibility (χ_M) was corrected for the sample holder and for the diamagnetic contribution of all the atoms using Pascal's tables. The ac susceptibility was measured with an oscillating ac field of 3 Oe in the frequency range from 1 to 1500 Hz.

Synthesis. *Preparation of 8-Hydroxyquinoline-2-carbaldehyde.* The following procedure was used for the preparation of the title compound. This procedure is a modification of a previously published synthesis method. In a two-necked round-bottomed flask, freshly sublimed selenium dioxide (6.66 g, 60 mmol) was taken in 150 mL of dioxane at 60 °C. To this, 2-methylquinolin-8-ol (5.2 g, 30 mmol) dissolved in dioxane (200 mL) was added dropwise over a period of 2.5 h and was refluxed at 95 °C for 24 h. The reaction mixture was cooled and filtered through Celite; dioxane was removed from the filtrate under reduced pressure. The residue was purified by column chromatography using silicagel (100 to 200 mesh) with 5:95 v/v ethylacetate-n-hexane used as the eluant to give a light-yellowish compound, 8-hydroxyquinoline-2-carbaldehyde. Yield = 4.15 g (80%). Mp = 90 °C. Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.27; H, 4.13; N, 8.21. ^1H NMR ($CDCl_3$, δ) 7.28 (d, 1H), 7.42 (d, 1H), 7.61 (t, 1H), 8.04 (d, 1H), 8.31(d, 1H), 10.20 (s, 1H). ESI-MS m/z (M + H): 174.06.

Preparation of Methyl 6-(hydroxymethyl) Picolinate. The preparation of methyl 6-(hydroxymethyl) picolinate was carried out by a slightly modified procedure upon comparison to a previously published synthesis method. $NaBH_4$ (2.03 g, 53.85 mmol, 1.5 equiv) was added in small portions over a period of 1 h to a stirred suspension of dimethylpyridine-2,6-dicarboxylate (6.0 g, 35.9 mmol) in methanol (150 mL) at 0 °C. This mixture was stirred at room temperature for another 3 h, and then methanol was removed in a rotary evaporator. A saturated $NaHCO_3$ aqueous solution (200 mL) was added to the residue, and the resulting aqueous solution was extracted with chloroform (5 × 100 mL). The combined organic layers

Scheme 1. The Synthesis of the LH$_3$ Ligand with Two Distinct Chelating Coordination Sites
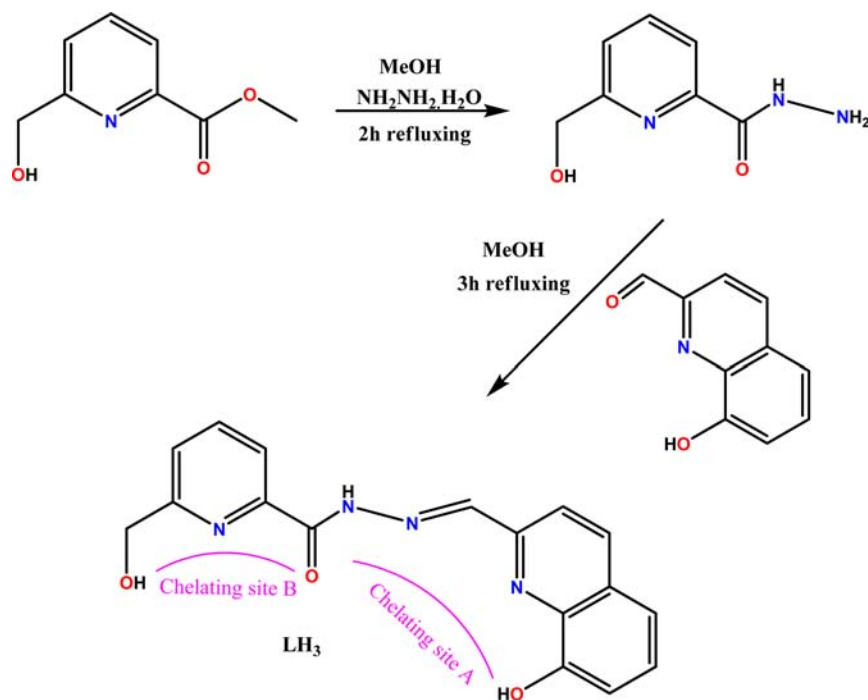
were dried (NaSO$_4$), filtered, and concentrated in vacuo to dryness. The resulting crude residue was purified by column chromatography (1:1 v/v *n*-hexane/EtOAc followed by 1:2 v/v of the same) and afforded the desired product (4.22 g, 82.2%) as a white solid. Anal. Calcd for C$_8$H$_9$NO$_3$: C, 57.5; H, 5.4; N, 8.4. Found: C, 56.9; H, 5.3; N, 8.3. Mp = 88 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.95 (d, 1H, pyr−*H*), 7.79 (t, 1H, pyr−*H*), 7.55 (d, 1H, pyr−*H*), 4.83 (s, 2H, methylene−*H*), 4.31 (s, 1H, -O*H*), 3.92 (s, 3H, methyl−*H*). IR: 1740 ν(C=O); 1591 ν(C=N)$_{py}$ cm^{-1}. ESI-MS *m/z* (M + H): 168.0658.

Preparation of 6-(Hydroxymethyl) Picolinohydrazide. A methanolic solution (40 mL) of methyl 6-(hydroxymethyl) picolinate (2.00 g, 11.96 mmol) was added dropwise to a stirred solution of hydrazine hydrate (3 mL, 59.82 mmol, 5 equiv) in methanol (60 mL) at room temperature. The reaction mixture was then heated under reflux for 2 h, cooled to room temperature, and kept in a refrigerator at 5 °C for crystallization. A white needle-shaped crystalline product was obtained, filtered under suction, washed with a small amount of cold methanol, and air dried. Yield = 1.87 g (93.53%). Anal. Calcd for C$_7$H$_9$N$_3$O$_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.02; H, 5.16; N 24.86. Mp = 110 °C. ^{1}H NMR (400 MHz, CD$_3$OD, δ) 7.92 (d, 2H, pyr−*H*), 7.58 (t, 1H, pyr−*H*), 4.72 (s, 2H, methylene−*H*). IR: 3407, 3303 ν(N−H); 1655 ν(C=O); 1571 ν(C=N)$_{py}$ cm^{-1}. ESI-MS *m/z* (M + H): 168.0772.

Preparation of (6-Hydroxymethyl)-N′-((8-hydroxyquinolin-2-yl)-methylene) Picolinohydrazide (LH$_3$). A methanolic solution (50 mL) of 8-hydroxyquinoline-2-carbaldehyde (1.13 g, 6.5 mmol) was added dropwise to a stirred solution of 6-(hydroxymethyl) picolinohydrazide (1.09 g, 6.5 mmol) in methanol (100 mL) in a 250 mL round-bottomed flask at room temperature. The reaction mixture was then heated under reflux for 3 h and slowly allowed to come to room temperature. The precipitate that formed was filtered, washed with diethyl ether, and dried. Yield = 1.57 g (75%). Anal. Calcd for C$_{17}$H$_{14}$N$_4$O$_3$: C, 63.35; H, 4.38; N, 17.38. Found: C, 63.57; H, 4.67; N, 17.77. Mp = 90 °C. ^{1}H NMR (500 MHz, [(CD$_3$)$_2$SO], δ) 12.36 (s, 1H, phenolic−O*H*), 9.80 (s, 1H, N*H*), 8.82 (s, 1H, imine-*H*), 7.10−8.33 (8H, Ar-*H*), 4.71 (s, 2H, −CH$_2$). ESI-MS *m/z* (M + H): 323.33.

Preparation of the Tetranuclear Complexes [{(LH)$_2$Dy$_4$}(μ_2-O)$_4$](H$_2$O)$_8$·2CH$_3$OH·8H$_2$O (1) and [{(LH)$_2$Ho$_4$}(μ_2-O)$_4$](H$_2$O)$_8$·6CH$_3$OH·4H$_2$O (2). The syntheses of 1 and 2 were carried out with the following general procedure. LH$_3$ (0.05g, 0.155 mmol) was dissolved in a mixture of methanol (10 mL) and dichloromethane

(15 mL), affording a colorless solution. Two equiv of LnCl$_3$·6H$_2$O (Ln = Dy or Ho) was added, and the color of the solution immediately became deep red. The reaction mixture was stirred at room temperature for 10 min, followed by the dropwise addition of 3 equiv of triethylamine. The reaction mixture was stirred at room temperature for 20 h, filtered, and kept for crystallization. After about 15 days, the slow evaporation of the mother liquor resulted in block-shaped deep red-colored crystals that were suitable for X-ray crystallography. The quantity of the reactants used in each reaction and the characterization data for compounds 1 and 2 are given below.

[{(LH)$_2$Dy$_4$}(μ_2-O)$_4$](H$_2$O)$_8$·2CH$_3$OH·8H$_2$O (1). DyCl$_3$·6H$_2$O (0.117 g, 0.31 mmol), LH$_3$ (0.050 g, 0.155 mmol), and Et$_3$N (0.047 g, 0.465 mmol). Yield = 72 mg (55%, based on Dy). Mp > 250 °C. IR (KBr) (cm^{-1}): 3643 (w), 3602 (w), 3361 (s), 1634 (w), 1590 (m), 1571 (w), 1546 (m), 1521 (s), 1498 (m), 1443 (w), 1425 (m), 1382 (m), 1324 (s), 1298 (m), 1103 (m), 1045 (w), 737 (m). Anal. Calcd for C$_{36}$H$_{64}$Dy$_4$N$_8$O$_{28}$ (1706.93): C, 25.33; H, 3.78; N, 6.56. Found: C, 25.07; H, 3.3; N, 6.96.

[{(LH)$_2$Ho$_4$}(μ_2-O)$_4$](H$_2$O)$_8$·6CH$_3$OH·4H$_2$O (2). HoCl$_3$•6H$_2$O (0.118 g, 0.31 mmol), LH$_3$ (0.050 g, 0.155 mmol), and Et$_3$N (0.047 g, 0.465 mmol). Yield = 70 mg (51%, based on Ho). Mp > 250 °C. IR (KBr) (cm^{-1}): 3643 (w), 3601 (w), 3361 (s), 1634 (w), 1590 (m), 1571 (w), 1543 (m), 1521 (s), 1498 (m), 1441 (w), 1426 (m), 1383 (m), 1324 (s), 1298 (m), 1103 (m), 1045 (w), 737 (m). Anal. Calcd for C$_{40}$H$_{72}$Ho$_4$N$_8$O$_{28}$ (1772.76): C, 27.10; H, 4.09; N, 6.32. Found: C, 26.37; H, 3.7; N, 6.66.

X-ray Crystallography. The crystal data and the cell parameters for 1 and 2 are given in Table 1. Single crystals suitable for X-ray analysis were grown by the slow evaporation of the mother liquor that contained a mixture of methanol and dichloromethane. The X-ray diffraction data for 1 and 2 were collected with a SMART CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å). The following programs were used. SMART[30] was used for collecting frames of data, indexing reflections, and determining lattice parameters; SAINT[30] was used for the integration of the intensity of reflections and scaling; SADABS[31] was used for the absorption correction; SHELXTL[32] was used for the space group and structure determination and for the least-squares refinement on F^2. The structures were solved with direct methods using the program SHELXS-97[33] and refined by full-matrix least-squares methods against F^2 using the program SHELXL-97. The hydrogen atoms were fixed at calculated positions, and their positions

were refined with a riding model. All of the hydrogen atoms of the water molecule that is coordinated to the lanthanide ions, all of the hydrogen atoms of the noncoordinated water molecules of both complexes **1** and **2**, the hydrogen atoms of the one methanol (complex **2**, solvent of crystallization), and the hydrogen atom on the oxygen atom of the −CH₂OH group (complex **2**) could not be located; these were included in the molecular formula directly. The figures were generated using Diamond 3.1e software.[34] Complexes **1** and **2** crystallized in the triclinic $P\bar{1}$ space group. The asymmetric unit of these complexes contains one-half of the molecule.

■ RESULTS AND DISCUSSION

Synthesis Aspects. The multidentate ligand (6-hydroxymethyl)-N'-((8-hydroxyquinolin-2-yl)methylene)-picolinohydrazide (LH₃) was prepared in about 75% yield by the condensation of 6-(hydroxymethyl) picolinohydrazide and 8-hydroxyquinoline-2-carbaldehyde (Scheme 1). The ESI-MS of LH₃ revealed a parent ion peak at m/z 323.33 (Supporting Information, Figure S1).

LH₃ can exist in different tautomeric forms, which upon deprotonation can afford $[LH]^{2-}$ possessing (Supporting Information, Figure S1) two distinct chelating coordination pockets that were expected to accommodate two lanthanide metal ions (Scheme 1). Accordingly, the reaction of LH₃ with 2 equiv of LnCl₃·6H₂O [Ln = Dy(III) or Ho(III)] in the presence of 3 equiv of triethylamine afforded the tetranuclear complexes **1** and **2** in reasonable yields: $[\{(LH)_2Ln_4\}(\mu_2\text{-}O)_4][H_2O]_8·xCH_3OH·yH_2O$, where for **1**, Ln = Dy(III), $x = 2$, $y = 8$, and for **2**, Ln = Ho(III), $x = 6$, $y = 4$ (Scheme 2). In these complexes, each $[LH]^{2-}$ binds to the two lanthanide metal ions

Scheme 2. The Synthesis of the Tetranuclear Complexes 1 and 2[a]

Ln= Dy(III) (1) ; Ho(III) (2)
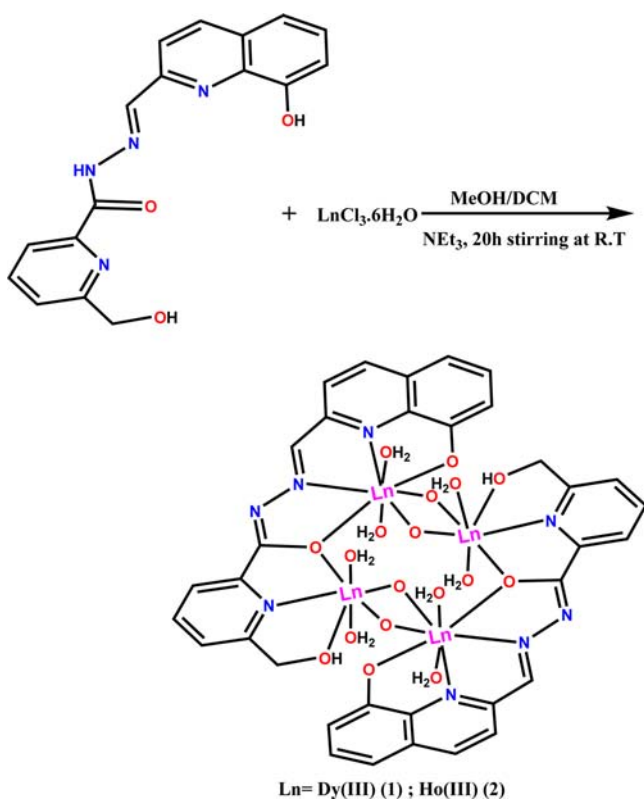
[a]The solvents that were present in the crystallization of **1** and **2** are not shown.

through a unique ONNONO donor action (Scheme 2). The formation of the tetranuclear complexes is facilitated by the μ-O bridges between the two pairs of lanthanide centers within the two dinuclear subunits.

X-ray Crystal Structures of 1 and 2. Complexes **1** and **2** were crystallized in the triclinic crystal lattice system in the centrosymmetric $P\bar{1}$ space group with $Z = 1$. The asymmetric unit contains one-half of the molecule. **1** and **2** are isostructural except for the variation in the number of lattice solvent molecules. Therefore, only the molecular structure of **1** is discussed herein. Some of the figures relating to the molecular structure of **1** are given in the Supporting Information (Figures S2, S3, and S4a,b). The details of the structure of **2** are also presented in the Supporting Information (Figures S5−S7). Selected bond distances of **1** are summarized in the caption of Figure 1. The other bond parameters of **1** and **2** are given in the Supporting Information (Tables S1 and 2).

The molecular structure of **1** is shown in Figure 1 and reveals that it possesses two dinuclear subunits. Each subunit contains two different types of Dy(III) ions and is built by the chelating coordination action of the two parts of the $[LH]^{2-}$ ligand that binds in its tautomeric form (Supporting Information, Scheme S1). Thus, Dy1 is bound by a phenolate oxygen (O3), a pyridinic nitrogen (N4), an imino nitrogen (N3), and an enolate oxygen (O2) that arise from tautomerism during coordination. In contrast, Dy2 is bound by an O2, a pyridinic nitrogen N1, and a CH₂OH (O1). The mode of coordination of the ligand in **1** is shown in Supporting Information, Chart S1.

The two subunits of **1** are joined to each other by oxido bridges, resulting in the formation of two Dy₂O₂ four-membered rings. Finally, all of the dysprosium centers have two coordinated water molecules. Because of this collective coordination behavior, Dy1 is eight-coordinate (2N, 6O). The evaluation of the polyhedral shape of the two Dy(III) centers was ascertained by continuous shape measures analysis that was carried out with SHAPE.[35] The geometry around Dy1 reveals that its closest ideal geometry is dodecahedron. However, its effective shape is distorted and is somewhere among triangular dodecahedron (DD), snub disphenoid (SD), and bicapped trigonal prism (BTP) (Supporting Information, Figure S4a). In contrast, Dy2 is seven-coordinate (1N,6O). The shape for the heptacoordinated Dy2 appears to be far from any reference geometry. This is rather uncommon and may reflect the steric constraint of the immediate coordination sphere that faces the bridging OH of the adjacent Dy−Dy moiety (Supporting Information, Figure S4b). An interesting aspect of the molecular structure of **1** is that all four of the dysprosium ions and all of the coordinating atoms of the $[LH]^{2-}$ ligand lie in the same plane (Supporting Information, Figure S2). To the best of our knowledge, this is a unique structural feature observed among all of the Dy₄ assemblies. The coordinated water molecules lie nearly perpendicular to the plane discussed above. Another interesting aspect of the structure of **1** is that 12 metal-containing ring systems (10 five-membered (a) Dy1−O3−C17−C13−N4; (b) Dy1−N4−C9−C8−N3; (c) Dy1−N3−N2−C7−O2; (d) Dy2−O2−C7−C6−N1; and (e) Dy2−N1−C2−C1−O1, and two four-membered Dy2−O4−Dy2′−O5) are generated as a result of the fusion of the two dinuclear subunits through the two Dy₂O₂ bridges. Last, the four dysprosium ions are present in the corners of a perfect rhombus with the inter Dy−Dy distances being 3.79(13) Å (Supporting
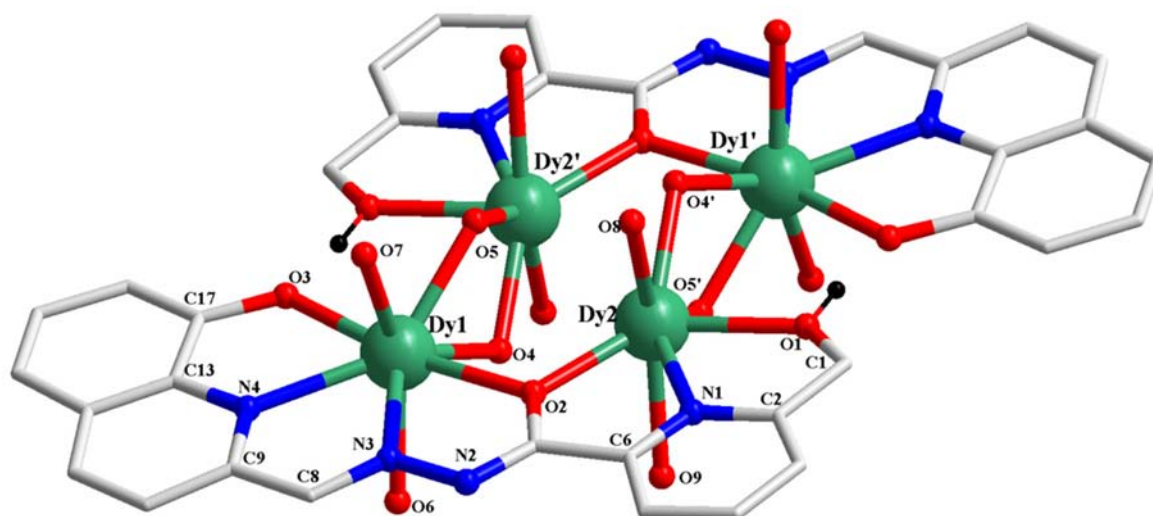
Figure 1. Molecular structure of **1**. The hydrogen atoms and the noncoordinated solvent molecules have been omitted for clarity. Selected bond distances (Å): Dy1−O2, 2.381(8); Dy1−O3, 2.306(9); Dy1−O4, 2.293(13); Dy(1)−O(5) 2.29(2); Dy1−O6, 2.371(11); Dy1−O7, 2.416(10); Dy1−N3, 2.562(10); Dy1−N4, 2.455(10); Dy2−O1, 2.352(9); Dy2−O2, 2.328(8); Dy2−O4$^{\#1}$, 2.258(14); Dy2−O5$^{\#1}$, 2.29(2); Dy2−O8, 2.468(12); Dy2−O9, 2.400(14); Dy2−N1, 2.537(10). Selected bone angles (deg): O4−Dy1−O5, 62.1(7); O4−Dy2'−O5, 62.03(5); O5$^{\#1}$−Dy2−O4'$^{\#1}$, 62.03(5); O5$^{\#1}$−Dy1$^{\#1}$−O4'$^{\#1}$, 62.1(7)

Information, Figure S3), and the diagonal Dy−Dy distances are 6.664(2) and 3.636(2) Å.

Magnetic Properties. The temperature dependence of the molar magnetic susceptibility, χ_M, has been investigated for **1** and **2** between 2 and 300 K, and the results are given as the $\chi_M T$ versus T plot in Figure 2. For **1**, the value of 53.4 cm³
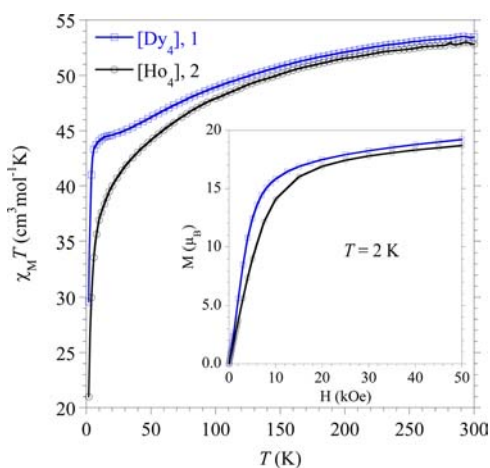

Figure 2. Temperature dependence of $\chi_M T$ for **1** and **2**. (Inset) Field dependence of the magnetization (solid lines are a guide for the eye).

mol⁻¹ K at 300 K is slightly lower than the value of 56.7 cm³ mol⁻¹ K that was anticipated for four uncoupled Dy(III) ions ($^6H_{15/2}$, $S = ^5/_2$, $L = 5$, $J = ^{15}/_2$, $g = ^4/_3$).[13] As the temperature is lowered, the $\chi_M T$ steadily decreases to reach a small plateau at ca. 44.5 cm³ mol⁻¹ K between 20 and 10 K before dropping steeply to reach 29.6 cm³ mol⁻¹ K at 2 K. For **2**, a $\chi_M T$ of 53.0 cm³ mol⁻¹ K was found at 300 K, which is slightly below the theoretical value of 56.28 cm³ mol⁻¹ K that was anticipated for four noninteracting Ho(III) ions ($^5I_8$, $S = 2$, $L = 6$, $J = 8$, $g_J = ^5/_4$).[38] The $\chi_M T$ continuously decreases when the temperature is reduced with a more rapid fall below 30 K, reaching 21.0 cm³ mol⁻¹ K at 2 K. Such overall behavior is characteristic of

Dy(III) and Ho(III) ions and results from the crystal field effects.[13] Therefore, it is difficult to conclude whether exchange interactions are occurring between the Ln(III) centers.[36] However, it is clear that even if such interactions are present they are very weak. The field dependence of the magnetization has been investigated in the range of 0 to 50 kOe at several temperatures from 2 to 10 K. In Figure 2 (inset), we show the behavior at 2 K, whereas that for the other T values are in Supporting Information, Figures S8a,b, and S9a,b. A rapid increase is observed for weak fields followed by a smoother but continuous increase to reach, for 50 kOe magnetizations, 19.2μB and 18.7μB for **1** and **2**, respectively. The saturation of the magnetization is not reached, which is consistent with the significant magnetic anisotropy of these Ln(III) centers and possibly with low-lying excited states. This is supported by the nonsuperposition of the M = f(H/T) curves (Supporting Information, Figures S8c, S9c). Notice also that the M = f(H) curves for **1** and **2** do not exhibit an S shape. This excludes the occurrence of weak antiferromagnetic intra- or intermolecular interactions.

The ac susceptibility data provided evidence of a slow-relaxing magnetization for **1** but not for **2**, even in the presence of an applied field (Supporting Information, Figure S10). Below 20 K, the out-of-phase component, χ_M'', for **1** deviates from zero and both χ_M' and χ_M'' become frequency-dependent. A peculiar feature of these curves is that they show two peaks that are frequency-dependent (Figure 3) with maxima for χ_M'' at 3.9 and 10.7 K for 1490 Hz, revealing the occurrence of two relaxation processes. This behavior has been described in recent reports[11,12b,15a,b,18c,20a,37,38] and is attributed to the presence of two Ln(III) sites in the crystal lattice. This applies to **1**, which possesses two Dy(III) units with distinct coordination spheres and geometries. Because of the very weak coupling between the Dy(III) centers, they may behave independently and are characterized by their own temperature of blockage of magnetization. The peaks of the χ_M'' signal can then be associated with two relaxation times corresponding to each of the two types of Dy(III) ions of **1**. The analysis of the Argand plots (Supporting Information, Figure S11) revealed that the α
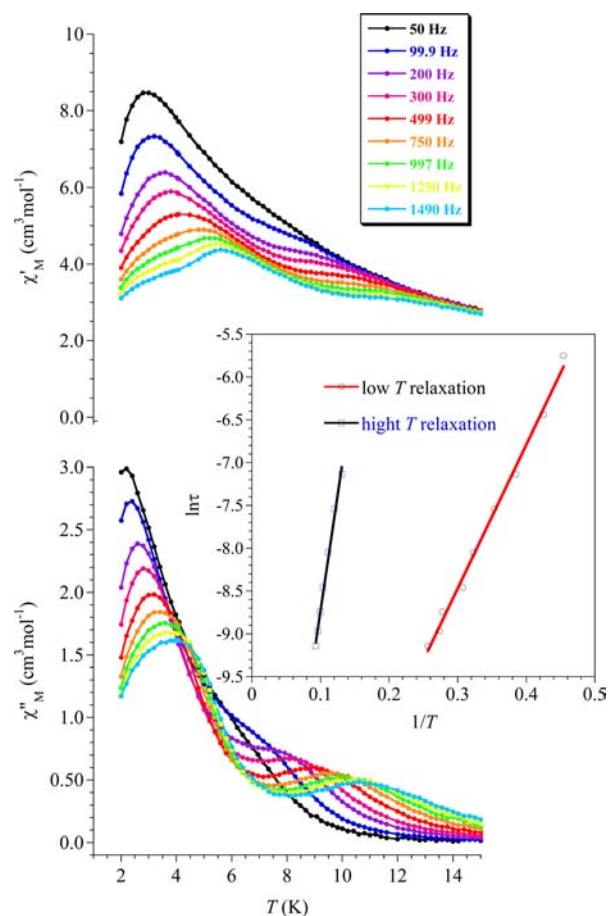
Figure 3. Temperature dependence of χ_M' and χ_M'' as a function of the frequency for **1**. (Inset) Plot of $\ln\tau$ vs $1/T_B$ and the straight line is a fit to the data points yielding $\Delta/k_B = 16.8$ K and $\tau_0 = 1.4 \times 10^{-6}$ s for the LT relaxation, and $\Delta/k_B = 54.2$ K and $\tau_0 = 7.2 \times 10^{-7}$ s for the HT relaxation. See the text.

parameter is close to zero (a single relaxation process) for the relaxation that was found in the temperature range from 8 to 12 K, whereas α increases for temperatures below 8 K in agreement with a wide distribution of τ. The evaluation of the effective energy barriers for magnetization reversal and relaxation times for both the low-temperature (LT) and high-temperature (HT) features have been deduced from the plot of the respective blocking temperatures (i.e. the maximum of χ_M'' for a given frequency) as $\ln\tau$ versus $1/T_B$, where $\tau = 1/(2\pi\nu)$ is the corresponding relaxation time for a given frequency ν. The straight lines in the inset of Figure 3 are the fits to the data points and are the signature of the thermal activation that is taking place following the Arrhenius law: $\tau = \tau_0 e^{\Delta/k_BT}$. The values obtained from the least-squares fitting are $\Delta/k_B = 16.8$ K and $\tau_0 = 1.4 \times 10^{-6}$ s for the LT relaxation and $\Delta/k_B = 54.2$ K and $\tau_0 = 7.2 \times 10^{-7}$ s for the HT relaxation. These values are in agreement with the SMM behavior for **1**. Interestingly, the difference between the effective energy barriers is significant, underlining the effect of the coordination of Dy(III). A tentative assignment of the geometry for the higher blocking temperature would be octacoordinated Dy1. Indeed, several examples of Dy(III) SMMs with rather high energy barriers have been found with eight-coordinated surroundings,[12b,15a,38] whereas lower energy barriers have been observed for heptacoordinated Dy(III) compounds.[39] The difference in the magnetic behavior of the Dy(III) and Ho(III) compounds in

the present study may be related to the crystal field splitting energy diagrams of these ions. For Dy(III), the energy between the lowest m_J and the first-excited m_J states is usually larger than for Ho(III).[40] Moreover, Dy(III) is a Kramer ion and therefore always has degenerate $\pm m_J$ states, which is not the case for compounds containing Ho(III), except in some instances.[13,41] Although many Dy(III)-based SMMs are known, very few Ho(III) derivatives have been found that exhibit a slow relaxation of their magnetization. The magnetic behavior of the compounds reported in the present study is consistent with such literature observations.

■ CONCLUSIONS

We have shown the successful design and assembly of a new family of tetranuclear, neutral, homometallic Ln^{III}_4 complexes that are characterized by a rhombus-shaped core topology. This was achieved using a new unsymmetrical hexadentate Schiff base hydrazide ligand. These centrosymmetric tetranuclear compounds contain two nonequivalent Ln(III) ions in their structures. Although the geometry around one type of Ln(III) ion is that of a distorted dodecahedron, the other type of Ln(III) is heptacoordinated and has a geometry that appears to be far from any reference geometry. In addition, compounds **1** and **2** represent the first examples of a homometallic 4f SMM family in which all of the donor atoms of the ligands and the metal ions are in a single perfect plane. The magnetization studies involving the ac susceptibility measurements revealed that between compounds **1** and **2** only the former exhibits a slow relaxation of magnetization below 20 K. A peculiar feature of the χ_M'' versus temperature (T K) curve of this compound is that it show two peaks that are frequency-dependent, revealing the occurrence of two relaxation processes that lead to two energy barriers (16.8 and 54.2 K) and time constants ($\tau_0 = 1.4 \times 10^{-6}$ s, $\tau_0 = 7.2 \times 10^{-7}$ s). This behavior is attributed to the presence of two Dy(III) sites with distinct coordination spheres and geometries. Because of the very weak coupling between the Dy(III) centers, they behave independently and are characterized by their own energies of blockage of magnetization. Given the versatility of the LH_3 ligand, we plan to modulate its structural features and to study its influence on the formation of other types of structurally diverse homonuclear 4f families.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Different forms of the ligand under different pH conditions, binding mode of the ligand LH_3 in its $[LH]^{2-}$, ESI-MS spectrum of the ligand (LH_3), planar arrangement of the four Dy(III) ions along with the coordinating atoms of the ligand LH^{2-}, rhombus-shaped Dy_4 core of **1**, distorted dodecahedral coordination environment around Dy1 in **1**, coordination environment around Dy2 in **1**, molecular structure of **2**, a view of the tetranuclear core of **2**, rhombus-shaped core of complex **2**, M versus H curves for **1**, M versus H curves for **2**, temperature dependence of $\chi M'$ and $\chi M''$ as a function of the frequency for **2**, Cole−Cole plots for **1**, important bond angle and bond parameters for complex **1**, important bond angle and bond parameters for complex **2**, and the crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: vc@iitk.ac.in (V.C.), sutter@lcc-toulouse.fr (J.-P.S.).

Notes

■ ACKNOWLEDGMENTS

■ REFERENCES
(1) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (b) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (c) Christou, G. *Polyhedron* **2005**, *24*, 2065. (d) Bai, Y.-L.; Tao, J.; Wernsdorfer, W.; Sato, O.; Huang, R.-B.; Zheng, L.-S. *J. Am. Chem. Soc.* **2006**, *128*, 16428. (e) Kajiwara, T.; Nakano, M.; Kaneko, Y.; Takaishi, S.; Ito, T.; Yamashita, M.; Igashira-Kamiyama, A.; Nojiri, H.; Ono, Y.; Kojima, N. *J. Am. Chem. Soc.* **2005**, *127*, 10150. (f) Costes, J.-P.; Clemente-Juan, F.; Dahan, J. M. *Inorg. Chem.* **2004**, *43*, 8200. (g) Escuer, A.; Vlahopoulou, G.; Mautner, F. A. *Inorg.Chem.* **2011**, *50*, 2717. (h) Ding, M.; Wang, B.; Wang, Z.; Zhang, J.; Fuhr, O.; Fenske, D.; Gao, S. *Chem.—Eur. J.* **2012**, *18*, 915. (i) Miyasaka, H.; Madanbashi, T.; Sugimoto, K.; Nakazawa, Y.; Wernsdorfer, W.; Sugiura, K.-I.; Yamashita, M.; Coulon, C.; Clérac, R. *Chem.—Eur. J.* **2006**, *12*, 7028. (j) Feng, X.; Harris, T. D.; Long, J. R. *Chem. Sci.* **2011**, *2*, 1688. (k) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (l) Jiang, S.-D.; Liu, S.-S.; Zhou, L.-N.; Wang, B.-W.; Wang, Z.-M.; Gao, S. *Inorg. Chem.* **2012**, *51*, 3079. (m) Beedle, C. C.; Henderson, J. J.; Ho, P.-C.; Sayles, T.; Nakano, M.; O'Brien, J. R.; Heroux, K. J.; Barco, E. D.; Maple, M. B.; Hendrickson, D. N. *Inorg. Chem.* **2010**, *49*, 5780.

(2) (a) Bogani, L.; Wernsdorfer, W. *Nat. Mater.* **2008**, *7*, 179. (b) Jo, M.-H.; Grose, J. E.; Baheti, K.; Deshmukh, M. M.; Sokol, J. J.; Rumberger, E. M.; Hendrickson, D. N.; Long, J. R.; Park, H.; Ralph, D. C. *Nano Lett.* **2006**, *6*, 2014. (c) Stefano, S. *Chem. Soc. Rev.* **2011**, *40*, 3336. (d) Filippo, T.; Affronte, M. *Chem. Soc. Rev.* **2011**, *40*, 3119.

(3) (a) Zheng, Y.-Z.; Evangelisti, M.; Winpenny, R. E. P. *Chem. Sci.* **2011**, *2*, 99. (b) Zheng, Y.-Z.; Evangelisti, M.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 3692. (c) Zheng, Y.-Z.; Pineda, E. M.; Helliwell, M.; Winpenny, R. E. P. *Chem.—Eur. J.* **2012**, *18*, 4161. (d) Zheng, Y.-Z.; Evangelisti, M.; Tuna, F.; Winpenny, R. E. P. *J. Am. Chem. Soc.* **2012**, *134*, 1057.

(4) (a) Cornia, A.; Mannini, M.; Sainctavit, P.; Sessoli, R. *Chem. Soc. Rev.* **2011**, *40*, 3076. (b) Tejada, J.; Chudnovsky, E. M.; del Barco, E.; Hernandez, J. M.; Spiller, T. P. *Nanotechnology* **2001**, *12*, 181. (c) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789. (d) Clemente-Leon, M.; Soyer, H.; Coronado, E.; Mingotaud, C.; Gomez-García, C. J.; Delhaes, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 2842. (e) Clemente-León, M.; Soyer, H.; Mingotaud, C.; Gómez-García, C. J.; Coronado, E.; Delhaes, P. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 669.

(5) (a) Mannini, M.; Pineider, F.; Danieli, C.; Totti, F.; Sorace, L.; Sainctavit, P.; Arrio, M. A.; Otero, E.; Joly, L.; Cezar, J. C.; Cornia, A.; Sessoli, R. *Nature* **2010**, *468*, 417. (b) Gonidec, M.; Biagi, R.; Corradini, V.; Moro, F.; Renzi, V. D.; Pennino, U. D.; Summa, D.; Muccioli, L.; Zannoni, C.; Amabilino, D. B.; Veciana, J. *J. Am. Chem. Soc.* **2011**, *133*, 6603. (c) Urdampilleta, M.; Klyatskaya, S.; Cleuziou, J. P.; Ruben, M.; Wernsdorfer, W. *Nat. Mater.* **2011**, *10*, 502. (d) Candini, A.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Affronte, M. *Nano Lett.* **2011**, *11*, 2634.

(6) (a) Feng, P. L.; Koo, C.; Henderson, J. J.; Manning, P.; Nakano, M.; Barco, E. D.; Hill, S.; Hendrickson, D. N. *Inorg. Chem.* **2009**, *48*, 3480. (b) Brechin, E. K.; Boskovic, C.; Wernsdorfer, W.; Yoo, J.; Yamaguchi, A.; Sanudo, E. C.; Concolino, T. R.; Rheingold, A. L.; Ishimoto, H.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2002**, *124*, 9710. (c) Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830. (d) Mishra, A.; Wernsdorfer, W.;

Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 15648. (e) Li, M.; Lan, Y.; Ako, A. M.; Wernsdorfer, W.; Anson, C. E.; Buth, G.; Powell, A. K.; Wang, Z.; Gao, S. *Inorg. Chem.* **2010**, *49*, 1158.

(7) (a) Lecren, L.; Wernsdorfer, W.; Li, Y.-G.; Vindigni, A.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2007**, *129*, 5045. (b) Lecren, L.; Roubeau, O.; Coulon, C.; Li, Y.-G.; Goff, X. F. L.; Wernsdorfer, W.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 17353. (c) Lecren, L.; Roubeau, O.; Li, Y.-G.; Goff, X. F. L.; Miyasaka, H.; Richard, F.; Wernsdorfer, W.; Coulona, C.; Clérac, R. *Dalton Trans.* **2008**, 755.

(8) (a) Wernsdorfer, W.; Chakov, N. E.; Christou, G. *Phys. Rev. Lett.* **2005**, *95*, 37203. (b) Lecren, L.; Wernsdorfer, W.; Li, Y.-G.; Roubeau, O.; Miyasaka, H.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 11311. (c) Wernsdorfer, W.; Soler, M.; Christou, G.; Hendrickson, D. N. *J. Appl. Phys.* **2002**, *91*, 7164. (d) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133.

(9) (a) Hill, S.; Edwards, R. S.; Aliaga-Alcalde, N.; Christou, G. *Science* **2003**, *302*, 1015. (b) del Barco, E.; Kent, A. D.; Yang, E. C.; Hendrickson, D. N. *Phys. Rev. Lett.* **2004**, *93*, 157202. (c) Friedman, J. R.; Patel, V.; Chen, W.; Tolpygo, S. K.; Lukens, J. E. *Nature* **2000**, *406*, 43.

(10) (a) Yoshihara, D.; Karasawa, S.; Koga, N. *J. Am. Chem. Soc.* **2008**, *130*, 10460. (b) Boudalis, A. K.; Raptopoulou, C. P.; Abarca, B.; Ballesteros, R.; Chadlaoui, M.; Tuchagues, J.-P.; Terzis, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 432. (c) Klower, F.; Lan, Y.; Nehrkorn, J.; Waldmann, O.; Anson, C. E.; Powell, A. K. *Chem.—Eur. J.* **2009**, *15*, 7413. (d) Ferguson, A.; Parkin, A.; Sanchez-Benitez, J.; Kamenev, K.; Wernsdorfer, W.; Murrie, M. *Chem. Commun.* **2007**, 3473. (e) Chen, S.-Y.; Beedle, C.; Gan, P.-R.; Lee, G.-H.; Hill, S.; Yang, E.-C. *Inorg. Chem.* **2012**, *51*, 4448. (f) Wu, D.; Guo, D.; Song, Y.; Huang, W.; Duan, C.; Meng, Q.; Sato, O. *Inorg. Chem.* **2009**, *48*, 854. (g) Ibrahim, M.; Lan, Y.; Bassil, B. S.; Xiang, Y.; Suchopar, A.; Powell, A. K.; Kortz, U. *Angew. Chem., Int. Ed.* **2011**, *50*, 4708. (h) Murugesu, M.; Raftery, J.; Wernsdorfer, W.; Christou, G.; Brechin, E. K. *Inorg. Chem.* **2004**, *43*, 4203. (i) Jurca, T.; Farghal, A.; Lin, P.-H.; Korobkov, I.; Murugesu, M.; Richeson, D. S. *J. Am. Chem. Soc.* **2011**, *133*, 15814.

(11) (a) Chandrasekhar, V.; Pandian, B. M.; Vittal, J. J.; Clérac, R. *Inorg. Chem.* **2009**, *48*, 1148. (b) Chandrasekhar, V.; Pandian, B. M.; Boomishankar, R.; Steiner, A.; Clérac, R. *Dalton Trans.* **2008**, 5143. (c) Chandrasekhar, V.; Pandian, B. M.; Boomishankar, R.; Steiner, A.; Vittal, J. J.; Houri, A.; Clérac, R. *Inorg. Chem.* **2008**, *47*, 4918. (d) Chandrasekhar, V.; Pandian, B. M.; Azhakar, R.; Vittal, J. J.; Clerac, R. *Inorg. Chem.* **2007**, *46*, 5140. (e) Liu, Y.; Chen, Z.; Ren, J.; Zhao, X.-Q.; Cheng, P.; Zhao, B. *Inorg. Chem.* **2012**, *51*, 7433. (f) Colacio, E.; Ruiz, J.; Mota, A. J.; Palacios, M. A.; Cremades, E.; Ruiz, E.; White, F. J.; Brechin, E. K. *Inorg. Chem.* **2012**, *51*, 5857. (g) Mereacre, V.; Ako, A. M.; Clérac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem.—Eur. J.* **2008**, *14*, 3577. (h) Ferbinteanu, M.; Kajiwara, T.; Choi, K.-Y.; Nojiri, H.; Nakamoto, A.; Kojima, N.; Cimpoesu, F.; Fujimura, Y.; Takaishi, S.; Yamashita, M. *J. Am. Chem. Soc.* **2006**, *128*, 9008.

(12) (a) Lin, P.-H.; Burchell, T. J.; Clérac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848. (b) Lin, P. H.; Burchell, T. J.; Ungur, L.; Chibotaru, L. F.; Wernsdorfer, W.; Murugesu, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9489. (c) Long, J.; Habib, J. F.; Lin, P.-H.; Korobkov, I.; Enright, G.; Ungur, L.; Wernsdorfer, W.; Chibotaru, L. F.; Murugesu, M. *J. Am. Chem. Soc.* **2011**, *133*, 5319. (d) Ma, Y.; Xu, G.-F.; Yang, X.; Li, L.-C.; Tang, J.; Yan, S.-P.; Cheng, P.; Liao, D.-Z. *Chem. Commun.* **2010**, *46*, 8264.

(13) (a) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369. (b) *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; Wiley-Interscience: New York, 1976. (c) Sutter,J.-P.; Kahn, M. L. *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2005; Vol.5, pp 161−188.

(14) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.-Y.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694.

(15) (a) Jiang, S.-D.; Wang, B.-W.; Su, G.; Wang, Z.-M.; Gao, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7448. (b) Jiang, S.-D.; Wang, B.-W.;

Sun, H.-L.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2011**, *133*, 4730. (c) Li, D.-P.; Wang, T.-W.; Li, C.-H.; Liu, D.-S.; Li, Y.-Z.; You, X.-Z. *Chem. Commun.* **2010**, *46*, 2929.

(16) (a) Sulway, S. A.; Layfield, R. A.; Tuna, F.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. Commun.* **2012**, *48*, 1508. (b) Yi, X.; Bernot, K.; Pointillart, F.; Poneti, G.; Calvez, G.; Daiguebonne, C.; Guillou, O.; Sessoli, R. *Chem.—Eur. J.* **2012**, *18*, 11379.

(17) (a) Hewitt, I. J.; Lan, Y.; Anson, C. E.; Luzon, J.; Sessoli, R.; Powell, A. K. *Chem. Commun.* **2009**, 6765. (b) Lin, S.-Y.; Zhao, L.; Guo, Y.-N.; Zhang, P.; Guo, Y.; Tang, J. *Inorg. Chem.* **2012**, *51*, 10522.

(18) (a) Anwar, M. U.; Thompson, L. K.; Dawe, L. N.; Habib, F.; Murugesu, M. *Chem. Commun.* **2012**, *48*, 4576. (b) Ke, H.; Xu, G.-F.; Guo, Y.-N.; Gamez, P.; Beavers, C. M.; Teat, S. J.; Tang, J. *Chem. Commun.* **2010**, *46*, 6057. (c) Guo, Y.-N.; Xu, G.-F.; Gamez, P.; Zhao, L.; Lin, S.-Y.; Deng, R.; Tang, J.; Zhang, H.-J. *J. Am. Chem. Soc.* **2010**, *132*, 8538. (d) Guo, P.-H.; Liu, J.-L.; Zhang, Z.-M.; Ungur, L.; Chibotaru, L. F.; Leng, J.-D.; Guo, F.-S.; Tong, M.-L. *Inorg. Chem.* **2012**, *51*, 1233.

(19) (a) Blagg, R. J.; Muryn, C. A.; McInnes, E. J. L.; Tuna, F.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 6530. (b) Blagg, R. J.; McInnes, E. J. L.; Tuna, F.; Winpenny, R. E. P. *Chem. Commun.* **2011**, *47*, 10587. (c) Peng, J.-B.; Kong, X.-J.; Ren, Y.-P.; Long, L.-S.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem.* **2012**, *51*, 2186.

(20) (a) Hewitt, I. J.; Tang, J.; Madhu, N. T.; Anson, C. E.; Lan, Y.; Luzon, J.; Etienne, M.; Sessoli, R.; Powell, A. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 6352. (b) Xue, S.; Zhao, L.; Guo, Y.-N.; Zhang, P.; Tang, J. *Chem. Commun.* **2012**, *48*, 8946. (c) Guo, Y.-N.; Chen, X.-H.; Xue, S.; Tang, J. *Inorg. Chem.* **2012**, *51*, 4035. (d) Langley, S. K.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **2012**, *51*, 3947. (e) Tian, H.; Guo, Y.-N.; Zhao, L.; Tang, J.; Liu, Z. *Inorg. Chem.* **2011**, *50*, 8688.

(21) (a) Canaj, A. B.; Tzimopoulos, D. I.; Philippidis, A.; Kostakis, G. E.; Milios, C. J. *Inorg. Chem.* **2012**, *51*, 7451. (b) Sharples, J. W.; Zheng, Y.-Z.; Tuna, F.; McInnes, E. J. L.; Collison, D. *Chem. Commun.* **2011**, *47*, 7650.

(22) (a) Guo, Y.-N.; Chen, X.-H.; Xue, S.; Tang, J. *Inorg. Chem.* **2012**, *51*, 4035. (b) Yang, P.-P.; Gao, X.-F.; Song, H.-B.; Zhang, S.; Mei, X.-L.; Li, L.-C.; Liao, D.-Z. *Inorg. Chem.* **2011**, *50*, 720.

(23) Alexandropoulos, D. I.; Mukherjee, S.; Papatriantafyllopoulou, C.; Raptopoulou, C. P.; Psycharis, V.; Bekiari, V.; Christou, G.; Stamatatos, T. C. *Inorg. Chem.* **2011**, *50*, 11276.

(24) Westin, L. G.; Kritikos, M.; Caneschi, A. *Chem. Commun.* **2003**, 1012.

(25) Miao, Y.-L.; Liu, J.-L.; Li, J.-Y.; Leng, J.-D.; Ou, Y.-C.; Tong, M.-L. *Dalton Trans.* **2011**, 10229.

(26) Chandrasekhar, V.; Senapati, T.; Dey, A.; Das, S.; Kalisz, M.; Clerac, R. *Inorg. Chem.* **2012**, *51*, 2051.

(27) (a) Lin, P.-H.; Burchell, T. J.; Clérac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848. (b) Ma, Y.; Xu, G.-F.; Yang, X.; Li, L.-C.; Tang, J.; Yan, S.-P.; Cheng, P.; Liao, D.-Z. *Chem. Commun.* **2010**, *46*, 8264. (c) Habib, F.; Lin, P.-H.; Long, J.; Korobkov, I.; Wernsdorfer, W.; Murugesu, M. *J. Am. Chem. Soc.* **2011**, *133*, 8830. (j) Zhao, L.; Xue, S.; Tang, J. *Inorg. Chem.* **2012**, *51*, 5994. (d) Tian, H.; Zhao, L.; Guo, Y.-N.; Guo, Y.; Tang, J.; Liu, Z. *Chem. Commun.* **2012**, *48*, 708. (e) Yan, P.-F.; Lin, P.-H.; Habib, F.; Aharen, T.; Murugesu, M.; Deng, Z.-P.; Li, G.-M.; Sun, W.-B. *Inorg. Chem.* **2011**, *50*, 7059. (f) Anwar, M. U.; Tandon, S. S.; Dawe, L. N.; Habib, F.; Murugesu, M.; Thompson, L. K. *Inorg. Chem.* **2012**, *51*, 1028. (g) Lin, H.; Sun, W.-B.; Yu, M.-F.; Li, G.-M.; Yan, P.-F.; Murugesu, M. *Chem. Commun.* **2011**, *47*, 10993. (h) Guo, Y.-N.; Xu, G.-F.; Wernsdorfer, W.; Ungur, L.; Guo, Y.; Tang, J.; Zhang, H.-J.; Chibotaru, L. F.; Powell, A. K. *J. Am. Chem. Soc.* **2011**, *133*, 11948. (i) Ke, H.; Xu, G.-F.; Guo, Y.-N.; Gamez, P.; Beavers, C. M.; Teat, S. J.; Tang, J. *Chem. Commun.* **2010**, *46*, 6057.

(28) (a) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Eds. ELBS and Longman: London, 1989. (b) Williams, D. B. G.; Lawton, M. *J. Org. Chem.* **2010**, *75*, 8351. (c) Zeng, X.; Coquiére, D.; Alenda, A.; Garrier, E.; Prangé, T.; Li, Y.; Reinaud, O.; Jabin, I. *Chem.—Eur. J.* **2006**, *12*, 6393.

(29) Tallec, G.; Imbert, D.; Fries, P. H.; Mazzanti, M. *Dalton Trans.* **2010**, 9490.

(30) SMART & SAINT software reference manuals, version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.

(31) Sheldrick, G. M. *SADABS*, version 2.05; a software for empirical absorption correction; University of Göttingen: Göttingen, Germany, 2002.

(32) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker AXS Inc.: Madison, WI, 2001.

(33) Sheldrick, G. M. *SHELXL97*; program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.

(34) Bradenburg, K. *Diamond*, version 3.1e; Crystal Impact GbR: Bonn, Germany, 2005.

(35) (a) *SHAPE*, version 2.0; continuous shape measures calculation; Electronic Structure Group, Universitat de Barcelona: Barcelona, Spain, 2010 (b) Casanova, D.; Llunell, M.; Alemany, P.; Alvarez, S. *Chem.—Eur. J.* **2005**, *11*, 1479.

(36) (a) Sutter, J.-P.; Kahn, M. L.; Kahn, O. *Adv. Mater.* **1999**, *11*, 863. (b) Kahn, M. L.; Sutter, J.-P.; Golhen, S.; Guionneau, P.; Ouahab, L.; Kahn, O.; Chasseau, D. *J. Am. Chem. Soc.* **2000**, *122*, 3413. (c) Datcu, A. N.; Roques, V.; Jubéra, I.; Imaz,Maspoch, D.; Sutter, J.-P.; Rovira, C.; Veciana, J. *Chem.—Eur. J.* **2011**, *17*, 3644. (d) Costes, J.-P.; Clemente, J.-M.; Dahan, F.; Nicodème, F. *Dalton Trans.* **2003**, 1272.

(37) (a) Guo, Y.-N.; Xu, G.-F.; Guo, Y.; Tang, J. *Dalton Trans.* **2011**, 9953. (b) Yang, F.; Yan, P.; Li, Q.; Chen, P.; Li, G. *Eur. J. Inorg. Chem.* **2012**, , 4287.

(38) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2931.

(39) (a) Liu, R.; Zhang, C.; Li, L.; Liao, D.; Sutter, J.-P. *Dalton Trans.* **2012**, 12139. (b) Yao, M.-X.; Zheng, Q.-Y.; Gao, F.; Li, Y. Z.; Song, Y.; Zuo, J.-L. *Dalton Trans.* **2012**, 13682.

(40) (a) Kahn, M. L.; Ballou, R.; Porcher, P.; Kahn, O.; Sutter, J.-P. *Chem.—Eur. J.* **2002**, *8*, 525. (b) Ishikawa, N.; Iino, T.; Kaizu, Y. *J. Phys. Chem. A* **2002**, *106*, 9543.

(41) (a) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *J. Am. Chem. Soc.* **2005**, *127*, 3650. (b) M.-E.; Boulon, G.; Cucinotta, J.; Luzon, C. D.; Innocenti, M.; Perfetti, K.; Bernot, G.; Calvez, A.; Caneschi, R.; Sessoli. *Angew. Chem., Int. Ed.* **2013**, *52*, 350.