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# Tetranuclear Lanthanide (III) Complexes Containing Dimeric Subunits: Single-Molecule Magnet Behavior for the Dy<sub>4</sub> Analogue

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**S** Supporting Information

**ABSTRACT:** The reaction of the lanthanide(III) salts [Dy(III), Tb(III), and Gd (III)] with a hetero donor chelating ligand N'-(2-hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl) picolinohydrazide (LH<sub>3</sub>) and pivalic acid (PivH) in the presence of tetran-butylammonium hydroxide (TBAH) afforded the tetranuclear Ln(III) coordination compounds,  $[Ln_4(LH)_2(LH_2)_2(\mu_2 - \mu_2)_2(\mu_2 - \mu_2)_2(\mu_2$  $\eta^{1}\eta^{1}\text{Piv}_{2}(\eta^{1}\text{Piv}_{4}) \cdot 2\text{CHCl}_{3}$  [Ln = Dy(1), Tb(2), and Gd(3)]. The molecular structure of these complexes reveals that the tetranuclear derivatives are composed of two dinuclear subunits which are interconnected through the coordination action of the picolinoyl hydrazine ligand. Within each subunit two different types of Ln(III) ions are present. One of these is eight-coordinate in a distorted triangular dodecahedral geometry while the other is



nine-coordinate in a distorted spherical capped square antiprism geometry. Alternating current (ac) susceptibility measurements of complex 1 reveal a frequency- and temperature-dependent two step out-of-phase signals under 1kOe DC field which is characteristic of a single-molecule magnet (SMM) behavior. Analysis of the magnetic data afforded the anisotropic barriers and relaxation times:  $\Delta/k_{\rm B} = 62.6$  K,  $\tau_0 = 8.7 \times 10^{-7}$  s;  $\Delta/k_{\rm B} = 26.3$  K,  $\tau_0 = 1.26 \times 10^{-6}$  s for the slow and fast relaxations respectively.

# INTRODUCTION

Research on lanthanide complexes has undergone a remarkable resurgence in the recent past. This is due to their potential applications in catalysis,<sup>1</sup> luminescence,<sup>2</sup> magnetic resonance imaging (MRI), or bioprobes for immunoassays.<sup>3</sup> In addition, considerable attention is also being bestowed on these compounds for investigating their magnetic properties such as single molecule magnet (SMM) behavior.<sup>4</sup> As is now reasonably well understood, SMM behavior is of molecular origin and can be seen in molecules that possess a high groundstate spin along with an intrinsic magnetic anisotropy.<sup>5</sup> Many lanthanide ions, particularly, Dy(III), Tb(III), or Er(III) seem to be suitable for this purpose. Because of this, either homometallic lanthanide complexes containing these ions or heterometallic 3d/4f complexes containing a combination of these lanthanide ions with appropriate transition metal ions have been receiving attention.<sup>6,7</sup> In particular, in recent years, there has been an upsurge of 4f-based polynuclear complexes for the development of higher energy-barrier SMMs as a result of the significant magnetic anisotropy of lanthanide ions arising from their large, unquenched orbital angular momentum.<sup>7</sup> A survey of literature reveals that homometallic lanthanide (III)based SMMs are being increasingly reported in literature, most

of them containing dysprosium(III) such as  $Dy_{2,}^{III} y_{2,}^{III} By_{3,}^{III} Dy_{3,}^{III} Dy_{4,}^{III} Dy_{5,}^{III} Dy_{6,}^{III} Dy_{7,}^{III} Dy_{8,}^{III} Dy_{9,}^{III} Dy_{9,}^{III} Dy_{9,}^{III} Dy_{9,}^{III} Dy_{9,}^{III} Dy_{1,1}^{III} Dy_{1,$ and so forth. Some examples of SMMs involving Tb(III),<sup>16</sup> Ho(III),<sup>17</sup> Er(III),<sup>18</sup> and Yb(III)<sup>18b,19</sup> are also known. Modulation of the nuclearity among polynuclear Ln(III) complexes is a synthetic challenge and has to be addressed by a proper design of the ligand systems. Recently our group has successfully assembled a variety of 3d-4f SMMs by using a phosphorus supported tris-hydrazone ligand.<sup>20</sup> However, the limitations of this ligand prompted us to look for an alternative design. By choosing a compartmental hydrazine ligand, which is not anchored on phosphorus, we were able to synthesize homometallic tetranuclear Dy(III) and Ho(III) complexes.<sup>10m</sup> Inspired by this, we extended this strategy by modifying the ligand to N'-(2-hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl) picolinohydrazide  $(LH_3)$  and also used an ancillary pivalate ligand. Accordingly, herein, we are reporting the synthesis of a new family of  $[Ln_4(LH)_2(LH_2)_2(\mu_2-\eta^1\eta^1Piv)_2-\eta^2\eta^2)$  $(\eta^1 \text{Piv})_4$ ]·2CHCl<sub>3</sub> complexes [Ln<sup>III</sup> = Dy(1), Tb(2), and

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#### Table 1. Crystal Data and Structure Refinement Parameters of 1-3

	1	2	3
formula	$C_{92}H_{110}Cl_6Dy_4N_{12}O_{28}$	$C_{92}H_{110}Cl_6Tb_4N_{12}O_{28}$	$C_{92}H_{110}Cl_6Gd_4N_{12}O_{28}$
M/g	2694.62	2680.30	2673.62
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	Pbca	Pbca	Pbca
a/Å	24.962(5)	25.0177(9)	25.250(4)
b/Å	15.241(5)	15.6762(6)	15.664(2)
c/Å	27.609(5)	27.8190(11)	27.906(4)
$\alpha = \beta = \gamma \; (\deg)$	90	90	90
$V/Å^3$	10504(4)	10910.1(7)	11037(3)
Ζ	4	4	4
$ ho_{ m c}/ m g~cm^{-3}$	1.704	1.632	1.609
$\mu/\mathrm{mm}^{-1}$	3.044	2.784	2.593
F(000)	5344	5328	5312
cryst size (mm <sup>3</sup> )	$0.052 \times 0.036 \times 0.019$	$0.053 \times 0.031 \times 0.017$	$0.081 \times 0.053 \times 0.035$
$\theta$ range (deg)	4.16 to 25.03	4.14 to 25.03	4.11 to 25.03
limiting indices	$-29 \le h \le 18$	$-29 \le h \le 22$	$-22 \le h \le 30$
	$-17 \le k \le 18$	$-13 \le k \le 18$	$-18 \le k \le 18$
	$-28 \le l \le 32$	$-26 \le l \le 33$	$-33 \le l \le 33$
reflns collected	52537	44285	72114
independent reflns	9229 [R(int) =0.0738]	9564 $[R(int) = 0.0594]$	9707 [ $R(int) = 0.1517$ ]
completeness to $\theta$ (%)	99.5	99.4	99.5
data/restraints/params	9229/4/657	9564/22/657	9707/4/657
goodness-of-fit on F <sup>2</sup>	1.049	1.051	0.998
final R indices $[I > 2\theta(I)]$	$R_1 = 0.0464$	$R_1 = 0.0402$	$R_1 = 0.0492$
	$wR_2 = 0.1128$	$wR_2 = 0.0858$	$wR_2 = 0.0887$
R indices (all data)	$R_1 = 0.0679$	$R_1 = 0.0774$	$R_1 = 0.1179$
	$wR_2 = 0.1257$	$wR_2 = 0.1039$	$wR_2 = 0.1085$
largest diff. peak and hole(e·Å^-3)	2.377 and -1.312	1.110 and -1.003	0.991 and -0.861

Gd(3)]. Detailed magnetic studies of these complexes are also reported.

# EXPERIMENTAL SECTION

Solvents and other general reagents used in this work were purified according to standard procedures.<sup>21</sup> Pyridine-2,6-dicarboxylic acid, sodium borohydride, Dy(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, and Gd-(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were obtained from Sigma Aldrich Chemical Co. and were used as received. Hydrazine hydrate (80%) and sodium sulfate (anhydrous) were obtained from SD. Fine Chemicals, Mumbai, India, and were used as such.

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating at 400-4000 cm<sup>-1</sup>. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>2</sub> CD<sub>2</sub>OD or CD<sub>3</sub>)<sub>2</sub>SO solutions on a JEOL JNM LAMBDA 400 model spectrometer operating at 400.0 MHz; Chemical shifts are reported in parts per million (ppm) and are referenced with respect to internal tetramethylsilane (1H).

Magnetic Measurements. Magnetic measurements were carried out with a Quantum Design MPMS 5S SQUID susceptometer 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 magnetic susceptibilities were measured in an applied field of 1000 Oe. The molar susceptibility  $(\chi_M)$  was corrected for sample holder and for the diamagnetic contribution of all the atoms by using Pascal's tables. AC susceptibility was measured with an oscillating ac field of 3 Oe using frequencies between 1 to 1500 Hz.

X-ray Crystallography. The crystal data for the compounds have been collected on a Bruker SMART CCD diffractometer (Mo K $\alpha$ radiation,  $\lambda = 0.71073$  Å). The program SMART<sup>22a</sup> was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT<sup>22a</sup> for integration of the intensity of reflections and scaling, SADABS<sup>22b</sup> for absorption correction, and SHELXTL<sup>22c,d</sup> for space group and structure determination and least-squares refinements on  $F^2$ . All the structures were solved by direct methods using the program SHELXS-97<sup>22e</sup> and refined by full-matrix least-squares methods against F<sup>2</sup> with SHELXL-97.<sup>22e</sup> Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic figures have been generated using Diamond 3.1e software.<sup>22f</sup> The crystal data and the cell parameters for compounds 1-3 are summarized in Table 1. CCDC-945440 (1), CCDC-945441 (2), and CCDC-945442 (3) contain crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

#### SYNTHESIS

Methyl 6-(Hydroxymethyl) Picolinate. The preparation of the title compound was carried out by a modification of a previously published method.<sup>23</sup> NaBH<sub>4</sub> (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 (6.00 g, 35.9 mmol) in MeOH (150 mL) at 0 °C. This mixture was stirred at room temperature for another 3 h and then MeOH was removed in a rotary evaporator. A saturated NaHCO<sub>3</sub> aqueous solution (200 mL) was added to the residue and the resulting aqueous solution was extracted with  $CHCl_3$  (5 × 100 mL). The combined organic layers were dried (anhydrous  $Na_2SO_4$ ), filtered, and concentrated in vacuo to dryness. The

resulting crude residue was purified by column chromatography (*n*-hexane/EtOAc; 1:1, then 1:2) giving the desired product (4.22 g, 82.17%) as a white solid. Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>NO<sub>3</sub>: C, 57.5; H, 5.4; N 8.4%. Found: C, 56.9; H, 5.3; N 8.3%. Mp: 88.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 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, -OH), 3.92 (s, 3H, methyl-H). IR (cm<sup>-1</sup>): 1740  $\nu$ (C=O); 1591  $\nu$ (C=N)<sub>py</sub>. ESI-MS (*m*/*z*): (M +H).168.0658.

6-(Hydroxymethyl) Picolinohydrazide. A methanolic solution 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. After the addition was over, the reaction mixture was heated under reflux for 2 h and subsequently allowed to come to room temperature before being kept in a refrigerator at 5 °C. A needle-shaped crystalline product was isolated which was suction-filtered, washed with a small amount of cold methanol, and air-dried. Yield 1.87 g (93.5%). Anal. Calcd. for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.02; H, 5.16; N 24.86. Mp: 110 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.92 (d, 2H, pyr-H), 7.58 (t, 1H, pyr-H), 4.72 (s, 2H, methylene-H).  $IR(cm^{-1})$ : 3407 and 3303  $\nu$ (N–H); 1655  $\nu$ (C=O); 1571  $\nu$ (C=N)<sub>pv</sub>. ESI-MS (m/ z): (M+H). 168.0772

N'-(2-hydroxy-3-methoxybenzylidene)-6-(hydroxymethyl) Picolinohydrazide (LH<sub>3</sub>). A 20 mL methanolic solution of o-vanillin (1.00 g, 6.50 mmol) was added dropwise to a stirred suspension of 6-(hydroxymethyl) picolinohydrazide (1.09 g, 6.50 mmol) in methanol (30 mL) at room temperature. The reaction mixture was heated under reflux for 3 h and allowed to come to room temperature where it was kept for 12 h without stirring. A precipitate formed was collected through filtration and washed with diethyl ether. Yield 1.82 g (92.9%). Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>: C, 59.79; H, 5.02; N, 13.95. Found: C, 60.04; H, 4.98; N, 13.95. Mp: 90 °C. <sup>1</sup>H NMR (400 MHz,  $[(CD_3)_2SO]$ ):  $\delta = 12.17$  (s, 1H, phenolic-OH), 10.94 (s, 1H, NH), 8.82 (s, 1H, imine-H), 8.02 (t, 1H, pyr-H), 7.96 (d, 1H, pyr-H), 7.69 (d, 1H, pyr-H), 7.11 (d, 1H, benz-H), 7.02 (d, 1H, benz-H), 6.86 (t, 1H, benz-H), 5.50 (s, 1H, -OH), 4.68(s, 2H, methylene-H), 3.78 (s, 3H, methoxy-H). IR (cm<sup>-1</sup>): 3416  $\nu$ (O–H); 3283  $\nu$ (N–H); 1672  $\nu$ (C=O); 1609  $\nu$ (C=N)<sub>imine</sub>; 1571  $\nu$ (C=N)<sub>py</sub>. ESI-MS (*m*/*z*): (M+H). 302.1148.

Tetranuclear Metal Complexes 1–3. The following general protocol was utilized for the preparation of the tetranuclear metal complexes. To a stirred solution of LH<sub>3</sub> in methanol (30 mL),  $Ln(NO_3)_3 \cdot xH_2O$  (for 1, 2, x = 5; 3, x = 6) was added. After this, tetra-n-butyl ammonium hydroxide (TBAH) (in 25% MeOH) was added dropwise and stirred for 15 min. Then, pivalic acid (PivH) was added. The reaction mixture was heated under reflux for 6 h, affording a clear yellow solution, allowed to come to room temperature, filtered, and the filtrate stripped off its solvent in vacuum affording a solid residue which was washed with diethyl ether and dried. The residue was dissolved in chloroform/acetonitrile (3:1) and kept for crystallization under slow evaporation conditions at room temperature. After 7–10 days, pure crystalline material suitable for X-ray diffraction was isolated. Specific quantities of the reactants involved in each reaction, yields of the products, and their characterization data are given below.

 $[Dy_4(LH)_2(LH_2)_2(\mu_2-\eta^1\eta^1Piv)_2(\eta^1Piv)_4]$ -2CHCl<sub>3</sub> (1). Quantities: LH<sub>3</sub> (0.072 g, 0.23 mmol), Dy(NO<sub>3</sub>)<sub>3</sub>-5H<sub>2</sub>O (0.104 g,

0.23 mmol), TBAH (0.62 mL, 0.57 mmol), PivH (0.036 g, 0.34 mmol). Yield: 0.065 g, 41.2% (based on Dy). Mp: 200 °C (d). IR (KBr)(cm<sup>-1</sup>): 3447(b), 3169(w), 2955(s), 1651(s), 1612(s), 1574(s), 1480(s), 1420(s), 1388(s), 1357(s), 1303(s), 1216(w), 1110(w), 1066(s), 1020(w), 997(w), 818(w), 791(s). Anal. Calcd for  $C_{92}H_{110}N_{12}O_{28}Cl_6Dy_4$  (2694.63): C, 41.01; H, 4.11; N, 6.26. Found: C, 40.86; H, 3.92; N, 6.42.

 $[Tb_4(LH)_2(LH_2)_2(\mu_2-\eta^1\eta^1Piv)_2(\eta^1Piv)_4]$ -2CHCl<sub>3</sub> (2). Quantities: LH<sub>3</sub> (0.072 g, 0.23 mmol), Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.103 g, 0.23 mmol), TBAH (0.62 mL, 0.57 mmol), PivH (0.036 g, 0.34 mmol). Yield: 0.072 g, 46.8% (based on Tb). Mp: 200 °C (d). IR (KBr) (cm<sup>-1</sup>): 3417(b), 3168(w), 2955(s), 1650(s), 1612(s), 1575(s), 1481(s), 1420(s), 1389(s), 1316(s), 1303(s), 1215(w), 1109(w), 1069(s), 1019(w), 999(w), 819(w), 790(s). Anal.Calcd for C<sub>92</sub>H<sub>110</sub>N<sub>12</sub>O<sub>28</sub>Cl<sub>6</sub>Tb<sub>4</sub> (2680.34): C, 41.23; H, 4.14; N, 6.27. Found: C, 40.81; H, 3.89; N, 6.38.

 $\begin{array}{l} [{\rm Gd}_4({\rm LH})_2({\rm LH}_2)_2(\mu_2-\eta^1\eta^1{\rm Piv})_2(\eta^1{\rm Piv})_4]\cdot 2{\rm CHCI}_3 \ (3). \ {\rm Quantities:} \ {\rm LH}_3 \ (0.072 \ g, \ 0.23 \ {\rm mmol}), \ {\rm Gd}({\rm NO}_3)_3\cdot {\rm 6H}_2{\rm O} \ (0.104 \ g, \ 0.23 \ {\rm mmol}), \ {\rm TBAH} \ (0.62 \ {\rm mL}, \ 0.57 \ {\rm mmol}), \ {\rm PivH} \ (0.036 \ g, \ 0.34 \ {\rm mmol}). \ {\rm Yield:} \ 0.065 \ g, \ 42.3\% \ ({\rm based \ on \ Tb}). \ {\rm Mp:} \ 200 \ ^{\circ}{\rm C} \ (d). \ {\rm IR} \ ({\rm KBr}) \ {\rm cm}^{-1}: \ 3425({\rm b}), \ 3166({\rm w}), \ 2955({\rm s}), \ 1651({\rm s}), \ 1612({\rm s}), \ 1574({\rm s}), \ 1481({\rm s}), \ 1420({\rm s}), \ 1386({\rm s}), \ 1355({\rm s}), \ 1308({\rm s}), \ 1215({\rm w}), \ 1112({\rm w}), \ 1067({\rm s}), \ 1017({\rm w}), \ 997({\rm w}), \ 818({\rm w}), \ 790({\rm s}). \ {\rm Anal.Calcd} \ {\rm for} \ \ C_{92}{\rm H}_{110}{\rm N}_{12}{\rm O}_{28}{\rm Cl}_6{\rm Gd}_4 \ \ (2673.62): \ C, \ 41.33; \ {\rm H}, \ 4.15; \ {\rm N}, \ 6.29. \ {\rm Found:} \ {\rm C}, \ 41.62; \ {\rm H}, \ 4.05; \ {\rm N}, \ 6.52. \end{array}$ 

# RESULTS AND DISCUSSION

Synthesis and Structural Characterization. Based on recent literature, it appears that multidentate Schiff base ligands are very effective in enabling the synthesis of polynuclear heterometallic  $3d/4f^{6c,e,f,i,j,20}$  and homometallic  $4f^{4d,8a,d,e,9c,10c,d,i,m,14d,24}$  complexes. Among these ligands, aroylhydrazone-based Schiff base ligands are particularly interesting in view of the presence of keto-enol tautomerism as well as the flexibility arising out of the conformational isomerism resulting from the C-C bond rotation.<sup>12c,24d</sup> Tang and co- workers have utilized the feature of keto-enol tautomerism to assemble and modulate the magnetic dynamics of Dy<sub>2</sub> complexes (Figure 1a). Although the beneficial feature of the conformational flexibility of the ligand was exploited to prepare the Dy<sub>2</sub> complex (Figure 1b), because of the lack of additional binding sites, cluster expansion does not occur in this case. On the other hand this group has synthesized a Dy<sub>6</sub> cluster by using a *o*-vanilloylhydrazone ligand,  $\{(N'-(amino-$ 



Figure 1. Some  $Dy_2$  complexes reported in the literature, prepared through the use ligands possessing the feature of Keto–Enol tautomerism. (a) A complex where the enol form of the ligand is involved in binding. (b) Utilization of keto–enol tautomerism and conformational isomerism in the formation of the dinuclear complex.<sup>24d</sup>



Figure 2.  $Dy_6$  complex known in the literature whose assembly involved the use of both keto-enol tautomerism as well as conformational isomerism of the ligand.<sup>12c</sup>

Scheme 1. Detailed Outline of the Synthesis of the Ligand (LH<sub>3</sub>)



(pyridin-2-yl)methylene)-*o*-vanilloylhydrazine)} where both the keto-enol tautomerism as well as conformational isomerism plays a vital role to link pairs of Dy<sub>3</sub> aggregate to extend the cluster size (Figure 2).<sup>12c</sup>

In this context it may be mentioned that Thompson and coworkers have utilized the feature of keto—enol tautomerism and conformational isomerism of ligands for preparing polynuclear complexes containing 3d-metal ions.<sup>25</sup>

With this background, we maneuvered the picolinoyl hydrazone part of the ligand by introducing a pendant  $-CH_2OH$  arm at the sixth position of the pyridine ring which generates an extra coordination pocket there by increasing the chances of increasing the nuclearity of the complex (Scheme 1).

Accordingly, the reaction of LH<sub>3</sub> with Ln(III) salts along with pivalic acid in the presence of tetra-*n*-butylammonium hydroxide afforded the tetranuclear complexes,  $[Ln_4(LH)_2(LH_2)_2(\mu_2-\eta^1\eta^1\text{Piv})_2(\eta^1\text{Piv})_4]\cdot 2\text{CHCl}_3$  [Ln = Dy(1), Tb(2) and Gd(3)] (Scheme 2). Single-crystal X-ray diffraction studies revealed that compounds 1–3 are isomorphous. They crystallize in the orthorhombic space group, *Pbca* with Z = 4. In view of their structural similarity only the structure of 1 will be described herein as a representative example. The structural diagrams of 2 and 3 are given in the Supporting Information, Figures S1 and S2. The detailed bond parameters for 1–3 are given in Supporting Information, Tables S1–S3.

A perspective view of the molecular structure of **1** is represented in Figure 3a. This reveals that the tetra nuclear complex contains two symmetrically related dinuclear subunits that are linked to each other by the intervention of two  $[LH_2]^-$ 

Scheme 2. Synthesis of the Homometallic  $Ln_4$  Complexes 1–3



ligands (Figure 3b). The asymmetric unit contains one-half of the molecules (Figure 3c). The two  $Dy^{III}$  ions within a given subunit are held together by phenolate and enolate oxygen atoms O7 and O2 respectively (Dy1-O7 = 2.362(4), Dy1-O2



Figure 3. (a) Molecular structure of 1. Hydrogen atoms (nonhydrogen bonded) and lattice chloroform molecules are omitted for clarity. To distinguish the keto and enol forms of the ligand a different color code for carbon has been chosen: pink color for the enol form and sky blue for the keto form. (b) A view of the pair of  $Dy_2$  cores covalently linked by two  $[LH_2]^-$  ligands. (c) Asymmetric unit of complex 1 (solvent molecule and hydrogen atoms are omitted for clarity).

= 2.343(4), Dy2-O7 = 2.355(4), Dy2-O2 = 2.377(4) Å). In addition, the pivalate ligand functions as a bridging ligand in a

 $\mu_2 \cdot \eta^1 \cdot \eta^1$  manner (Dy1-O9 = 2.304(5), Dy(2)-O(10) = 2.331(4) Å). To the best of our knowledge, this type of topology exhibited by 1 is new and has not been found among tetranuclear 3d or 4f complexes.

An interesting aspect of the assembly of the dinuclear subunit is that the ligand  $LH_3$ , as anticipated, functions in two different ways. In one way (Scheme 3, Ligand A) the ligand is present in the keto form  $[LH_2]^-$  and possesses 3 types of coordination pockets. While pockets II and III are utilized to hold the dinuclear unit, pocket III extends the cluster size. The other form of the ligand (Scheme 3, Ligand B) is present in the enolate form  $[LH]^{2-}$  and possesses two coordination pockets. Both of these are utilized for holding the two metal centers in the dinuclear part (Scheme 4). The coordination modes of these two forms of the ligand are depicted in Scheme 4. The Dy…Dy separation in the dinuclear unit is 3.851(9) Å.

Thus, to reiterate, the ligand utilizes both the phenomenon of the keto–enol tautomerism as well as its conformational flexibility (as a result of C–C rotation between C21–C22 or C6–C7 bonds) in the formation of 1. A comparison of the metric parameters found in the current instance along with a literature precedent is given in Table 2. The extended nuclearity of 1 arises from the presence of the additional –CH<sub>2</sub>OH binding site. Interestingly, this site functions in its neutral mode and does not get deprotonated under the reaction conditions.

As mentioned above, for these complexes, the two Ln(III) are octa- (70, 1N, Figure 4a) and nona-coordinated (60, 3N, Figure 4b). The evaluation of the polyhedral shapes of the two Ln(III) centers was ascertained by continuous shape measurement analysis that was carried out with SHAPE to ascertain the actual shape.<sup>27</sup> The eight-coordinated Ln1 center was found to exhibit a distorted coordination polyhedron that significantly deviates from ideal geometries and is somewhere among triangular dodecahedron (DD), square antiprism (SA) and biaugmented trigonal prism (BTP) (see Supporting Information, Table S4). For the nine-coordinated Ln2 center the geometry around the metal is distorted spherical capped square antiprism (Supporting Information, Table S4). The variation of the coordination geometry around the two Dy(III) centers has implications in their magnetic properties, particularly, the magnetic relaxation under ac susceptibility conditions as discussed below.

It may be mentioned, that in contrast to the current instance, where the two dinuclear sub units are connected to each other affording an overall tetranuclear ensemble, we have recently reported a compact tetranuclear complex by the use of a different ligand; the hydrazide motif is similar in the latter and in the ligand used in the current instance (Figure 5).

The X-ray crystal structure of **1** reveals the presence of intraand intermolecular hydrogen-bonding interactions (see Supporting Information, Table S5) to generate a one-dimensional supramolecular architecture with a zigzag arrangement of the molecules (see Supporting Information, Figure S3).

**IR Spectroscopy.** A detailed comparison of the IR data of the free ligand and the metal complexes is presented in Table 3 which reflects the coordination modes of the ligand in its two different forms (Ligand A and Ligand B). The IR spectrum of the ligand exhibits a band at 3283 cm<sup>-1</sup> due to the  $\nu_{(N-H)}$  stretching frequency, signifying its keto form in the solid state. This band is seen in all the complexes (1–3) around 3170 cm<sup>-1</sup>. The  $\nu_{(C=O)}$  of the free ligand is observed at 1672 cm<sup>-1</sup>; in the metal complexes this is shifted to a lower energy value

### Scheme 3. Conformational Isomerism of the Ligand LH<sub>3</sub> Showing Different Coordination Pockets



Scheme 4. Coordination Modes of the LH<sub>3</sub> with Various Deprotonated Forms Indicated by the Harris Notation<sup>26</sup>



(~1650 cm<sup>-1</sup>). The  $\nu_{(C=N)}$  vibration mode at 1609 cm<sup>-1</sup> in the spectrum of the free ligand remains unchanged in the complexes. However, the IR spectra of 1–3 reveals, a broad and strong peak around 1574 cm<sup>-1</sup>. This is attributed to the formation of the new C=N bond upon the deprotonation of the free N–H group of the ligand.

**Magnetic Properties.** The temperature dependence of  $\chi_M T$  ( $\chi_M$  stands for the molar magnetic susceptibility) for 1–3 between 2 and 300 K are plotted in Figure 6. For each compound, the values found at 300 K (i.e., 56.3, 47.0, and 31.1 cm<sup>3</sup> mol<sup>-1</sup> K respectively for 1–3) are in agreement with that anticipated for four Ln(III) ions in the absence of exchange interactions (i.e., 56.7 (Dy<sub>4</sub>), 47.2 (Tb<sub>4</sub>), and 31.5 cm<sup>3</sup> mol<sup>-1</sup> K (Gd<sub>4</sub>)) and decreases as *T* is lowered with a more rapid fall below 100 K. For 1 and 2 this behavior originates from the crystal field effects and possible exchange interactions <sup>28</sup> while for the Gd derivative only antiferromagnetic interactions, an analysis of the experimental behavior for 3 has been performed. Based on the structural features for this compound, the most likely exchange pathway between the Gd ions is through the O-



Figure 4. (a) Eight coordinate distorted geometry around the Dy1 ion. (b) Nine coordinate distorted coordination around the Dy2 ion.

bridge; the formylpyridine moiety linking two Gd dimers is not expected to mediate efficiently an exchange coupling. Therefore modeling was performed by considering two magnetically independent Gd2 units. Best fit to experimental data yielded  $J_{\text{GdGd}} = -0.12 \pm 0.07 \text{ cm}^{-1}$  (based on  $H = -JS_{\text{Gd1}} \cdot S_{\text{Gd2}}$ ) and  $g = -JS_{\text{Gd1}} \cdot S_{\text{Gd2}}$  $2.0 \pm 0.06$  (Figure 6). The strength found is in the order of the values usually found for related species.<sup>29</sup> It is indicative for very weak antiferromagnetic interactions taking place in these  $Ln_4$  compounds. This is confirmed by the field dependence of the magnetization for 3 (See Supporting Information, Figure S4) that reaches 27.3  $\mu_{\rm B}$  for 5 T, a value close to the anticipated saturation value  $Ms = 28 \ \mu_{\rm B}$ . We expect a nonmagnetic ground state for the Gd4 compound; however, according to the very weak antiferromagnetic interaction  $(-0.12 \text{ cm}^{-1})$  this state is reached only for temperatures below 0.5 K. At 2 K (the lowest T we can investigate) the excited states (i.e., the paramagnetic regime) still strongly contribute to the magnetic susceptibility, which accounts for the large  $\chi_{\rm M}T$  value observed.

Table 2. Comparison of Bond Lengths (Å) of the Keto-Enol Forms of the Ligands between Complexes Reported Here and Those Known from the Literature

	bond length				
complex	C–O (ketoform)	N–C (ketoform)	C–O (enolform)	N-C (enolform)	reference
$\mathrm{Dy}_4(\mathrm{LH})_2(\mathrm{LH}_2)_2(\mu_2\eta^1\eta^1\mathrm{Piv})_2(\eta^1\mathrm{Piv})_4\cdot 2\mathrm{CHCl3}\ \mathrm{LH}_3=N'-(2\text{-hydroxy-3-methoxybenzylidene})-6-(hydroxymethyl)$ picolinohydrazide	1.235(8)	1.346(9)	1.291(8)	1.295(8)	this work
$\label{eq:constraint} \begin{array}{l} [Dy_2(Hovph)(ovph)(NO_3)_2(H_2O)_4]\cdot NO_3\cdot 2CH_3OH\cdot 3H_2O \ H_2ovph = (2\text{-hydroxy-3-methoxybenzylidene}) \ picolinohydrazide \end{array}$	1.240(10)	1.323(11)	1.297(10)	1.315(10)	24d



Ln= Dy(III) and Ho(III)

Figure 5. Ln<sub>4</sub> complexes reported recently using a Schiff-base formed between the condensation of 6-(hydroxymethyl) picolinohydrazide and 8-hydroxyquinoline-2-carbaldehyde.<sup>10m</sup>

Table 3. IR Data  $(cm^{-1})$  of the Ligand and the Complexes 1-3



**Figure 6.** Temperature dependence of  $\chi_M T$  for  $\mathbf{1}$  ( $\mathbf{O}$ , Dy<sub>4</sub>),  $\mathbf{2}$  ( $\Box$ , Tb<sub>4</sub>) and  $\mathbf{3}$  ( $\bigcirc$ , Gd<sub>4</sub>). Calculated behavior (solid line) for  $J_{GdGd} = -0.12 \pm 0.07 \text{ cm}^{-1}$  and  $g = 2.0 \pm 0.06$  (see text).

AC susceptibility data revealed the occurrence of a slow relaxing magnetization for **1**. Below 20 K, an out-of-phase component,  $\chi_M''$ , is observed and both  $\chi_M'$  and  $\chi_M''$  are frequency dependent. The behavior recorded with a DC field of 1 kOe is depicted in Figure 7; the external field was applied to reduce the QTM at low temperature, but this does not affect the maxima for  $\chi_M'$  and  $\chi_M''$  found at higher temperatures (see Supporting Information, Figure S5). A salient feature of these curves are the occurrence of two peaks with maxima for  $\chi_M''$  at 5.7 and 12.8 K for 1450 Hz, revealing that two relaxation processes take place for this compound. Such a behavior can be ascribed to the presence of two Ln sites with different coordination spheres in **1**. Because of the absence, or too



**Figure 7.** AC susceptibility data for 1 recorded with DC field of 1 kOe. (top) Temperature dependence of  $\chi_{\rm M}'$  and  $\chi_{\rm M}''$  as a function of the frequency. (bottom) Plot of  $\ln \tau = f(1/T_{\rm B})$  and best fit (straight lines) of the Arrhenius law to the data point yielding  $\Delta/k_{\rm B} = 26.3$  K and  $\tau_0 = 1.3 \times 10^{-6}$  s for the LT relaxation and  $\Delta/k_{\rm B} = 62.6$  K and  $\tau_0 = 8.7 \times 10^{-7}$  s for the HT relaxation, see text.

weak, exchange interaction among them, they behave independently and exhibit each a characteristic relaxation of the magnetization. Such a behavior has been well documented in recent years<sup>8f</sup> and was also found for a related  $Dy_4$ compound we have reported recently.<sup>10m</sup> The analysis of the Argand plots<sup>5a</sup> (see Supporting Information, Figure S6) suggest a single relaxation process for the relation observed in the 9–15 K temperature range. For lower temperatures this is no longer the case because of the concomitant contributions of the two relaxation processes, hence leading to a wider distribution for the relaxation time.

An evaluation of the effective energy barriers for the magnetization reversal and relaxation times associated to the lower (LT) and higher temperature (HT) signals have been deduced from the plot of  $\ln \tau = f(1/T_B)$  where  $\tau$  is the relaxation time for a given frequency, i.e.  $(2\pi\nu)^{-1}$ , and  $T_B$  the blocking temperature (i.e., the *T* of the maxima of  $\chi_M^{"}$  for this frequency). Fitting the Arrhenius law  $\tau = \tau_0 e^{\Delta/k_B T}$  to the data points (Figure 7) lead to  $\Delta/k_B = 26.3$  K and  $\tau_0 = 1.3 \times 10^{-6}$  s for the LT relaxation, and  $\Delta/k_B = 62.6$  K and  $\tau_0 = 8.7 \times 10^{-7}$  s for the HT relaxation. These values are in agreement with a SMM behavior for 1.

The energy barriers obtained show the strong effect of the coordination sphere of the Dy ion on  $\Delta/k_{\rm B}$ . Following the

tentative assignment we have discussed in a previous case, <sup>10m</sup> it is likely that the larger barrier for reversal of magnetization is due to the octacoordinated Dy centers. Theoretical investigations devoted to anisotropic Ln ions suggest that the magnetization blocking barrier for these ions is very versatile; coordination geometry, ligand strengths, and their positioning in the coordination sphere as well as intercenter interactions play a prominent role.<sup>30</sup>

The energy barrier for magnetization reversal of  $\Delta/k_{\rm B} = 62.6$ K obtained here is fairly high as compared to the majority of Ln-based SMMs or SIMs. It is also larger by 8 K to the energy barrier obtained for octacoordinated DyIII in a distorted dodecahedral geometry with a very similar ligand set [the hydrazide part is common while the aldehyde part is 8hydroxyquinoline-2-carbaldehyde (Figure 5)]. It is interesting to compare the magnetic properties observed in the current instance with that of the tetranuclear rhombus-shaped dysprosium analogue, that was previously reported by us.<sup>10m</sup> The latter also showed two frequency-dependent peaks in the  $\chi_{\rm M}{}''$  vs temperature curves, indicating the occurrence of two relaxation processes that lead to two energy barriers (16.8 and 54.2 K) and time constants ( $\tau_0 = 1.3 \times 10^{-6}$  s,  $\tau_0 = 7.2 \times 10^{-7}$ s).<sup>10m</sup> This was related to the presence of two distinct geometrical sites (seven- and eight coordinated) for Dy(III) ions in rhombus Dy<sub>4</sub> complex. In the current instance also, although the complex is made up of two pairs of dimers, two energy barriers (26.3 and 62.6 K) and time constants ( $\tau_0 = 1.4$  $\times$  10<sup>-6</sup> s,  $\tau_0 = 8.7 \times 10^{-7}$  s) are obtained from their ac susceptibility studies. In both of these instances distinct coordination geometries, we believe, is responsible for the observation of two relaxation processes. These results are indicative of the importance of the geometrical features around the lanthanide ions in determining and differentiating their magnetic properties.

Finally, it can be seen that while 1 shows SMM behavior, 2 does not. This difference arises, presumably because Dy(III) is a Kramer ion and irrespective of the ligand field it is expected to possess a bistable ground state. On the other hand, Tb(III) ion is a non-Kramer ion and so its complex will have a bistable ground state only if it has an axially symmetrical ligand field.<sup>30d,31</sup>

# CONCLUSION

To summarize, we report the synthesis and structural characterization of tetranuclear lanthanide complexes that contain two symmetrical Ln(III) dimeric pairs. The assembly of these complexes has been accomplished by the use of a multisite coordination ligand containing distinct binding pockets. Magnetic studies on these complexes reveal the presence of SMM behavior for the Dy<sup>III</sup> analogue. Also, two relaxation processes with distinct energy barriers are seen for this complex which can be correlated to the difference in the geometrical parameters of the Dy<sup>III</sup> ions. Finally, the energy barrier found for the high-temperature relaxation process is notably larger than the values usually observed for multicenter Dy<sup>III</sup> SMMs.

#### ASSOCIATED CONTENT

### **Supporting Information**

Molecular structures of 2 and 3, details structural parameters for the compounds 1-3 and magnetic data for 1. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data in CIF format for 1-3 have been

deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 945440–945442. 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; http://www.ccdc.cam. ac.uk).

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# Notes

The authors declare no competing financial interest.

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