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# Tetranuclear Lanthanide(III) Complexes in a Seesaw Geometry: Synthesis, Structure, and Magnetism

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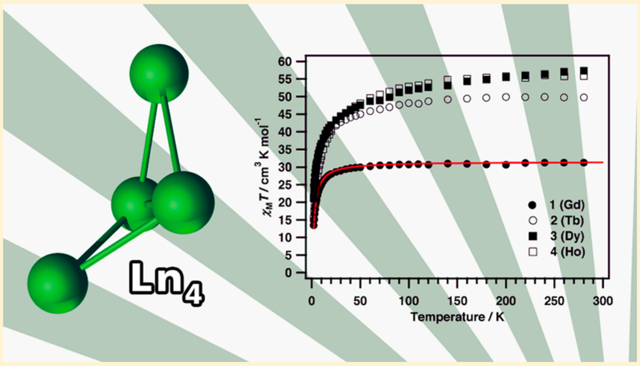
*Supporting Information*



**ABSTRACT:** The reaction of 2-methoxy-6-(pyridin-2-ylhydrazonomethyl)phenol (LH) with Ln(III) (Ln = Gd, Tb, Dy, Ho) salts in the presence of an excess of triethylamine afforded $[Gd_4(L)_4(\mu_4\text{-OH})(\mu_3\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 4CH_3CN\cdot CH_3OH\cdot 2H_2O$ (**1**), $[Tb_4(L)_4(\mu_4\text{-OH})(\mu_3\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 4CH_3CN\cdot 3H_2O$ (**2**), $[Dy_4(L)_4(\mu_4\text{-OH})(\mu_3\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 6CH_3CN\cdot H_2O$ (**3**), and $[Ho_4(L)_4(\mu_4\text{-OH})(\mu\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 8CH_3CN\cdot 3CH_3OH\cdot 2H_2O$ (**4**). All four complexes contain a monocationic tetranuclear core with a unique *seesaw* topology. The tetranuclear assembly is formed through the coordination of four $[L]^-$, one $\mu_4$-OH, two $\mu_3$-OH, and four chelating nitrate ligands, with a charge-balancing nitrate counteranion. Magnetic studies reveal a weak antiferromagnetic coupling throughout the series. Compound **1** can be modeled well with an isotropic exchange between all centers parametrized by $J = -0.09$ cm$^{-1}$. Compound **3** exhibits slow magnetic relaxation at low temperatures.

## ■ INTRODUCTION

Homometallic lanthanide complexes of varying nuclearities and topologies have attracted a lot of interest in recent years,[1] with potential applications in areas as diverse as catalysis,[2] luminescence,[3] imaging,[4] and molecular magnetism.[5] The discovery of single-molecule magnet (SMM) behavior[6] (and the qualitative understanding that a high ground-state spin combined with a large magnetic anisotropy are vital prerequisites[1,7]) has led to the routine examination of lanthanide complexes in search of this property.[1] As a result, many lanthanide complexes ranging over mono-,[8] di-,[9] tri-,[10] and polynuclear,[11] have become attractive synthetic targets for chemists. A large number of polymetallic Dy(III) systems have been structurally and magnetically characterized, and some of them have been found to exhibit SMM behavior. Although the specific orientations of the anisotropy axes at the individual ions is the principal factor in determining whether or not the metal cluster exhibits SMM behavior, exchange coupling between metals has also been found to affect the relaxation dynamics in some cases.[1] Unfortunately, control of these factors remains a big challenge. Recently, two oxo-bridged polymetallic lanthanide cages, $[Dy_5O(O^iPr)_{13}]$[12] and $[Dy_4K_2O(O^tBu)_{12}]$,[13] studied by one of us have been found to possess the highest energy barriers to magnetization reversal.

We have recently been involved in the use of polydentate Schiff base chelating ligands for the assembly of heterometallic 3d-4f[14] and homometallic 4f[15] complexes of different nuclearities and core topologies. Among these, a tetranuclear Dy(III) complex with a rhombus-shaped core topology was studied by ac susceptibility and was found to possess two distinct relaxation dynamics correlated to the two crystallographically different Dy(III) ions present in the structure. Spurred by this, we have been examining other polydentate ligands that could potentially allow the assembly of homometallic lanthanide complexes with different topologies.[16] A search of the literature revealed that the hydrazone Schiff base ligand, 2-methoxy-6-(pyridin-2-ylhydrazonomethyl)phenol (LH) has been used for the preparation of 3d[17] and 3d-4f[18] polynuclear metal complexes. The contiguous coordination units present within this ligand, namely a methoxy group, a phenolic unit, an imine, and a pyridyl nitrogen, make this ligand very suitable for the preparation of homometallic tetranuclear lanthanide complexes. Accordingly, herein, we report the synthesis and the structural/magnetic characterization of the first family of tetranuclear Ln(III) complexes assembled from the ligand LH, consisting of $[Gd_4(L)_4(\mu_4\text{-OH})(\mu_3\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 4CH_3CN\cdot CH_3OH\cdot 2H_2O$ (**1**), $[Tb_4(L)_4(\mu_4\text{-OH})(\mu_3\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 4CH_3CN\cdot 3H_2O$ (**2**), $[Dy_4(L)_4(\mu_4\text{-OH})(\mu_3\text{-OH})_2(NO_3)_4]\cdot(NO_3)\cdot 6CH_3CN\cdot$

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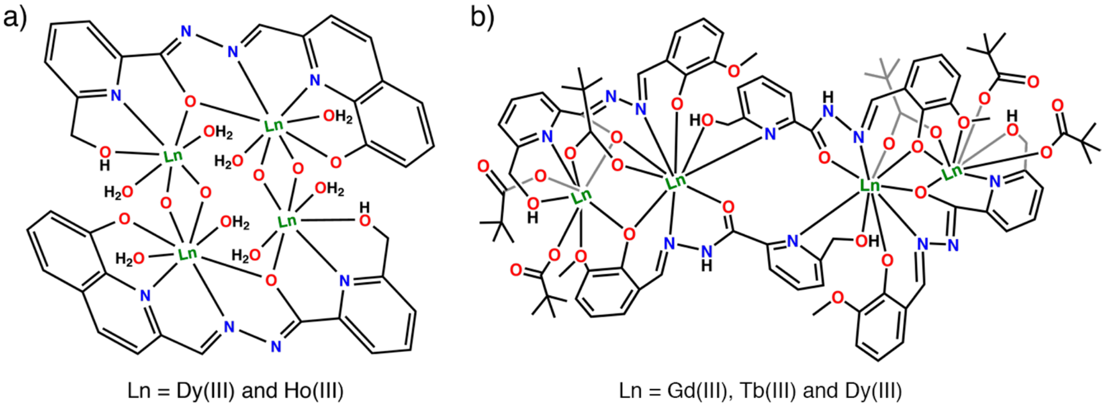
**Scheme 1. (a) A Tetrameric Lanthanide Complex in a Rhombus-Shaped Geometry. (b) A $Ln_4$ Complex Containing Two Dimeric Subunits**



Ln = Dy(III) and Ho(III)

Ln = Gd(III), Tb(III) and Dy(III)

$H_2O$ (**3**), and $[Ho_4(L)_4(\mu_4\text{-}OH)(\mu\text{-}OH)_2(NO_3)_4]\cdot(NO_3)\cdot 8CH_3CN\cdot 3CH_3OH\cdot 2H_2O$ (**4**).

## EXPERIMENTAL SECTION

**Reagents and General Procedures.** Solvents and other general reagents used in this work were purified according to standard procedures.[19] *o*-Vanillin (S. D. Fine Chemicals, Mumbai, India), 2-hydrazinopyridine, $Gd(NO_3)_3\cdot 6H_2O$, $Tb(NO_3)_3\cdot 5H_2O$, $Dy(NO_3)_3\cdot 5H_2O$, and $Ho(NO_3)_3\cdot 5H_2O$ were obtained from Sigma-Aldrich Co. and were used as received. The hydrazone Schiff base ligand 2-methoxy-6-(pyridin-2-ylhydrazonomethyl)phenol (LH) was prepared using a reported procedure.[20]

**Instrumentation.** Melting points were measured using a JSGW melting point apparatus and are uncorrected. $^1H$ NMR spectra were recorded in $CD_3OD$ solutions on a JEOL JNM LAMBDA 400 model spectrometer operating at 400 MHz. Chemical shifts are reported in parts per million (ppm) and are referenced with respect to internal tetramethylsilane ($^1H$). IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating at 400−4000 $cm^{-1}$. Elemental analyses of the compounds were obtained using a ThermoQuest CHNS-O EA/110. ESI-MS spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. All samples were subjected to variable temperature (2−300 K) dc magnetic susceptibility and variable field (0−7 T) magnetization measurements. Ac susceptibility measurements were also carried out over the temperature range 1.8−10 K with an ac field of strength 1.55 G oscillating at frequencies between 1 and 1400 Hz. All magnetic measurements were performed at the University of Manchester using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Diamagnetic corrections were calculated using Pascal's constants, and an experimental correction for the sample holder was applied.

**X-ray Crystallography.** Single-crystal X-ray structural studies of **1**−**4** were performed on a Bruker SMART APEX CCD diffractometer equipped with an Oxford low-temperature attachment. Data were collected using a graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The crystals did not degrade/decompose during the data collection. Data collection, structure solution, and refinement were performed using the SMART, SAINT, and SHELXTL programs, respectively.[21a−f] All of the non-hydrogen atoms were refined anisotropically using full-matrix least-squares procedures. All of the hydrogen atoms were fixed at idealized positions, and a riding model was used. The lattice solvent molecules of complex **4** ($8CH_3CN$ and $3CH_3OH$) could not be modeled satisfactorily due to the presence of heavy disorder. Therefore, the PLATON/SQUEEZE[21g,h] program was used to remove those disordered solvent molecules and gave a total electron count of 469 per unit cell, which corresponds to 234 electrons per molecule (Z = 2) and was assigned to $8CH_3CN$ and 3MeOH molecules (expected 230 electrons). After PLATON/SQUEEZE, a high "Q-peak" appears close to the metal center, which results in high $R_1$ and $WR_2$ factors for the refinement. Several attempts were made to recollect this data using different crystals, but the solvent disorder precluded a satisfactory model in all cases. All of the mean plane analyses and molecular drawings were obtained using Diamond (version 3.1).

**Synthesis.** *General Procedure for the Synthesis of 1*−*4*. The following general protocol was utilized for the preparation of the tetranuclear metal complexes. $Ln(NO_3)_3\cdot xH_2O$ (for **1**, $x$ = 6; for **2**, **3**, **4**, $x$ = 5) was added to a stirred solution of LH in methanol (30 mL). Triethylamine was then added dropwise, and the solution stirred for 12 h, affording a clear yellow solution. This solution was evaporated to dryness, redissolved in methanol−acetonitrile (1:1), and filtered. The filtrate was allowed to evaporate slowly at room temperature. After 4−5 days, yellow block-shaped crystals suitable for X-ray diffraction had formed. Specific quantities of the reactants involved in each reaction, yields of the products, and their characterization data are given below.

*$[Gd_4(L)_4(\mu_4\text{-}OH)(\mu_3\text{-}OH)_2(NO_3)_4]\cdot(NO_3)\cdot 4CH_3CN\cdot CH_3OH\cdot 2H_2O$ (**1**).* Quantities: LH (0.061 g, 0.251 mmol), $Gd(NO_3)_3\cdot 6H_2O$ (0.113 g, 0.251 mmol), $NEt_3$ (0.14 mL, 1.00 mmol). Yield: 0.066 g, 48% (based on Gd). Mp: 200 °C (d). IR (KBr) $cm^{-1}$: 3408(br), 1621(s), 1544(w), 1487(w), 1460(s), 1426(s), 1384(s), 1278(w), 1223(w), 1130(w), 1079(s), 1002(w), 971(w), 849(w), 770(w), 738(s), 415(w). Anal. Calcd for $C_{61}H_{71}Gd_4N_{21}O_{29}$ (2191.36): C, 33.43; H, 3.27; N, 13.42. Found: C, 33.16; H, 3.06; N, 13.22.

*$[Tb_4(L)_4(\mu_4\text{-}OH)(\mu_3\text{-}OH)_2(NO_3)_4]\cdot(NO_3)\cdot 4CH_3CN\cdot 3H_2O$ (**2**).* Quantities: LH (0.061 g, 0.251 mmol), $Tb(NO_3)_3\cdot 5H_2O$ (0.109 g, 0.251 mmol), $NEt_3$ (0.14 mL, 1.00 mmol). Yield: 0.072 g, 52% (based on Tb). Mp: 200 °C (d). IR (KBr) ($cm^{-1}$): 3434(br), 2924(s), 1621(s), 1572(s), 1543(w), 1485(s), 1462(s), 1426(s), 1384(s), 1350(s), 1284(s), 1241(s), 1222(w), 1171(w), 1153(w), 1126(s), 1081(s), 1003(w), 975(s), 891(w), 854(w), 772(s), 740(s), 627(w), 421(s). Anal. Calcd for $C_{60}H_{69}N_{21}O_{29}Tb_4$ (2184.04): C, 33.00; H, 3.18; N, 13.47. Found: C, 32.68; H, 2.94; N, 13.26.

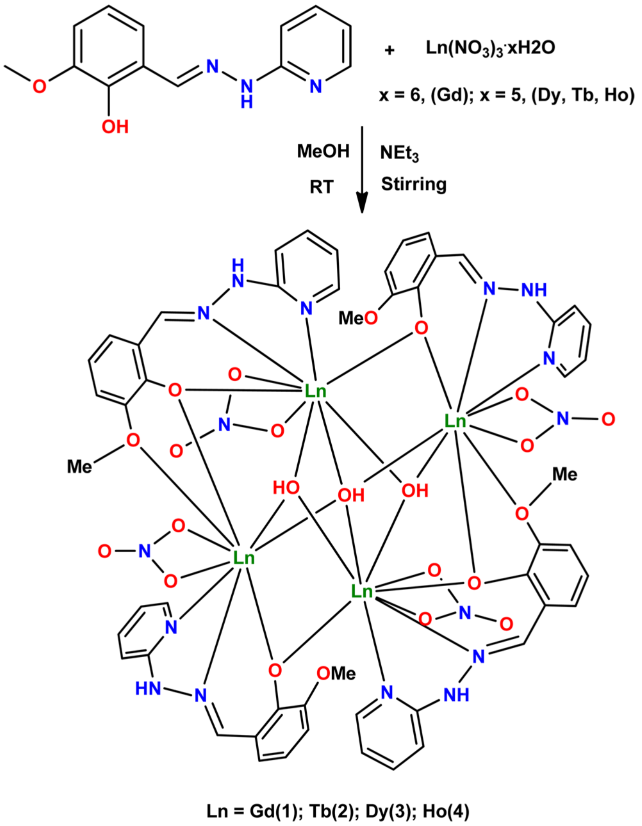
*$[Dy_4(L)_4(\mu_4\text{-}OH)(\mu_3\text{-}OH)_2(NO_3)_4]\cdot(NO_3)\cdot 6CH_3CN\cdot H_2O$ (**3**).* Quantities: LH (0.061 g, 0.251 mmol), $Dy(NO_3)_3\cdot 5H_2O$ (0.110 g, 0.251 mmol), $NEt_3$ (0.14 mL, 1.00 mmol).Yield: 0.076 g, 54% (based on Dy). Mp: 200 °C (d). IR (KBr) ($cm^{-1}$): 3420(br), 2925(w), 1621(s), 1577(s), 1546(w), 1487(s), 1462(s), 1427(s), 1383(s), 1351(s), 1285(s), 1243(s), 1222(s), 1171(w), 1155(w), 1128(s), 1080(s), 1001(w), 973(s), 890(w), 850(w), 770(s), 740(s), 646(s), 629(w), 422(s). Anal. Calcd for $C_{64}H_{71}Dy_4N_{23}O_{27}$ (2244.43): C, 34.25; H, 3.19; N, 14.35. Found: C, 33.86; H, 2.96; N, 14.09.

*$[Ho_4(L)_4(\mu_4\text{-}OH)(\mu\text{-}OH)_2(NO_3)_4]\cdot(NO_3)\cdot 8CH_3CN\cdot 3CH_3OH\cdot 2H_2O$ (**4**).* Quantities: LH (0.061 g, 0.251 mmol), $Ho(NO_3)_3\cdot 5H_2O$ (0.111 g, 0.251 mmol), $NEt_3$ (0.14 mL, 1.00 mmol). Yield: 0.078 g, 50% (based on Ho). Mp: 200 °C (d). IR (KBr) ($cm^{-1}$): 3419(br), 1620(s), 1542(w), 1486(s), 1461(s), 1426(w), 1384(s), 1277(w), 1223(w), 1131(w), 1078(s), 1004(w), 970(w), 850(w), 771(w), 739(w), 416(w). Anal. Calcd for $C_{73}H_{94}N_{26}O_{31}Ho_4$ (2491.40): C, 35.19; H, 3.80; N, 14.62. Found: C, 34.92; H, 3.54; N, 14.39.

## RESULTS AND DISCUSSION

**Synthesis.** As mentioned above, we recently reported a homonuclear $Ln_4$ family possessing a planar rhombus-shaped core using a compartmental hydrazone ligand (Scheme 1).[15a] A modification of this ligand, utilizing features such as conformational flexibility and keto−enol tautomerism, also afforded homometallic tetranuclear lanthanide complexes containing two dimeric subunits (Scheme 1).[16] In the current instance we have used the compartmental Schiff base ligand 2-methoxy-6-(pyridin-2-ylhydrazonomethyl)phenol (LH) for the preparation of homometallic tetranuclear lanthanide complexes (Scheme 2). The molecular geometries of these complexes have been ascertained by X-ray crystallography and are discussed below.

**Scheme 2. Synthesis of the Homometallic $Ln_4$ Complexes 1−4**



*Molecular Structures of 1−4.* The crystallographic parameters of **1−4** are given in Table 1. **1−4** are isostructural and crystallize in the triclinic system, $P\bar{1}$ ($Z = 2$). In view of the structural similarity of the compounds, only the representative structure will be described here. The detailed structural parameters of all four compounds are given in the Supporting Information.

The four lanthanide ions are arranged in a very unusual seesaw topology held together by four $(L)^-$, one ($\mu_4$-OH), and two ($\mu_3$-OH). Each lanthanide ion also possesses a single $\eta^2$-nitrate ligand, and the overall charge of the complex is balanced by a nitrate counteranion (Figure 1 and Scheme 2). The two edge-sharing triangular faces are capped on the convex side by the two $\mu_3$-hydroxides, while all four Ln (III) ions are bridged on the concave side by the $\mu_4$-hydroxide (Figure 2).

Inspection of the crystal packing of the molecules reveals the presence of intermolecular hydrogen-bonding interactions between the nitrate counteranions and the N−H group of the hydrazine motif to generate a two-dimensional supramolecular architecture (Supporting Information). The nature of the hydroxide ligands were confirmed by BVS calculations (Supporting Information).[22] Instances of $\mu_4$-OH are also found in $[Er_{14}(o\text{-}O_2NC_6H_4O)_{24}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}]$,[23] $[Dy_4(\mu_4\text{-}OH)(PTC_4A)_2Cl_3(CH_3OH)_2(H_2O)_3]{\cdot}4.7CH_3OH{\cdot}2H_2O$,[24] and $[Tb_9(\mu_4\text{-}O)(\mu_4\text{-}OH)(\mu_3\text{-}OH)_8(acac)_{16}{\cdot}4H_2O]$.[25]

The lanthanide ions that are bridged by the $(L)^-$ ligand are connected directly by the $\mu_2$-oxygen of the phenolate moiety, and indirectly by the binding of the oxygen on the OMe group of the *o*-vanillin moiety to one ion, and the nitrogens on the imine and pyridyl groups to the other (2.21110 using the Harris notation). In two of the $(L)^-$ bridges, the oxygen of the OMe group does not bind (2.20110 using the Harris notation). The coordination modes of the ligands are summarized in Chart 1.

Each Ln(III) center is nine-coordinate with a coordination sphere of $O_7N_2$. As mentioned above, two of the Ln(III) centers are ligated by the OMe group of $(L)^-$, while the other two are not. The coordination number of the latter ions is compensated by being bonded to both $\mu_3$-hydroxides, with the former ions being bonded to only one. Systematic analysis of the geometries using SHAPE 2.1[26] reveals that the individual Ln(III) are best described as capped square antiprism (Figure 3), with the distortion from ideal geometry being significantly greater in the dysprosium ions of compound **3** (CShM values of ∼23 compared to ∼2 for **1**, **2**, and **4**). The geometry of the tetrameric arrangement of the metal ions is confirmed to be very close to an idealized seesaw arrangement (CShM of ∼1) using the same approach. Full results of the geometric analyses are reported in the Supporting Information.

**Magnetic Properties.** The temperature dependence of the molar magnetic susceptibility, $\chi_M$, has been investigated for all four compounds under an applied magnetic field of 0.1 T, and the results are given as $\chi_M T$ versus $T$ in Figure 4. At room temperature, the $\chi_M T$ values of compounds **1−4** are 31.3, 49.7, 57.1, and 55.8 $cm^3\ K\ mol^{-1}$, respectively. These values are in good agreement with the expected theoretical values (**1**: 31.5; **2**: 47.3; **3**: 56.7; **4**: 56.3 $cm^3\ K\ mol^{-1}$) for four uncoupled lanthanide ions: Gd(III) ($^8S_{7/2}$, $S = 7/2$, $L = 0$, $g = 2$, $C = 7.88$ $cm^3\ K\ mol^{-1}$), Tb(III) ($^7F_6$, $S = 3$, $L = 3$, $g = 3/2$, $C = 11.82$ $cm^3\ K\ mol^{-1}$), Dy(III) ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17$ $cm^3\ K\ mol^{-1}$), and Ho(III) ($^5I_8$, $S = 2$, $L = 6$, $g = 5/4$, $C = 14.08$ $cm^3\ K\ mol^{-1}$). For **2−4**, $\chi_M T$ declines when the temperature is decreased as a result of single ion crystal-field effects. This effect is more pronounced below 50 K, where a drop in the $\chi_M T$ value to 24.8 $cm^3\ K\ mol^{-1}$ for $Tb_4$, 21.2 $cm^3\ K\ mol^{-1}$ for $Dy_4$, and 15.4 $cm^3\ K\ mol^{-1}$ for $Ho_4$ is observed, indicating the depopulation of the excited Stark sublevels of the Ln(III) ions. Weak antiferromagnetic coupling between metal centers can also contribute to this behavior but cannot be easily quantified in **2−4** because of the strong orbital momentum of the Ln(III) ions present. In compound **1**, however, the four Gd(III) ions do not show first order orbital momentum, meaning that the observed decrease of $\chi_M T$ below ca. 50 K is a direct consequence of antiferromagnetic exchange. In agreement with this, the molar magnetization ($M$) against field ($H$) for **1** is below the Brillouin curve calculated for four uncoupled Gd(III) ions with $S = 7/2$ and $g = 2$ (Supporting Information), which strongly suggests antiferromagnetic coupling between the Gd(III) centers. The variable temperature magnetic susceptibility (Figure 4) and the field-dependent magnetization behavior at 2 K and 4 K (Figure 5 and Supporting Information)

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

| compound | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| formula | $C_{61}H_{67}Gd_4N_{21}O_{29}$ | $C_{60}H_{63}N_{21}O_{29}Tb_4$ | $C_{64}H_{69}Dy_4N_{23}O_{27}$ | $C_{54}H_{49}Ho_4N_{18}O_{28}$ |
| formula weight | 2187.36 | 2178.04 | 2242.43 | 2057.84 |
| temp (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| crystal system | triclinic | triclinic | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| unit cell dimensions | | | | |
| $a$ (Å) | 13.972(5) | 13.966(5) | 13.995(5) | 14.239(5) |
| $b$ (Å) | 15.262(5) | 15.284(5) | 15.264(5) | 14.396(5) |
| $c$ (Å) | 20.028(5) | 19.802(5) | 19.910(5) | 21.642(5) |
| $\alpha$ (deg) | 95.272(5) | 95.728(5) | 96.262(5) | 99.618(5) |
| $\beta$ (deg) | 95.905(5) | 95.302(5) | 94.902(5) | 104.751(5) |
| $\gamma$ (deg) | 111.219(5) | 111.289(5) | 111.330(5) | 108.128(5) |
| volume (Å$^3$); $Z$ | 3922(2); 2 | 3881(2); 2 | 3902(2); 2 | 3928(2); 2 |
| density (mg m$^{-3}$) | 1.852 | 1.864 | 1.909 | 1.740 |
| absol coef (mm$^{-1}$) | 3.432 | 3.694 | 3.880 | 4.069 |
| $F$(000) | 2136 | 2124 | 2188 | 1982 |
| crystal size (mm) | 0.16 × 0.14 × 0.11 | 0.16 × 0.14 × 0.12 | 0.18 × 0.16 × 0.12 | 0.18 × 0.16 × 0.14 |
| $\theta$ range (deg) | 2.00 to 25.50 | 2.09 to 25.50 | 2.00 to 25.50 | 4.09 to 25.03 |
| limiting indices | $-12 \leq h \leq 16$ | $-16 \leq h \leq 16$ | $-16 \leq h \leq 16$ | $-16 \leq h \leq 16$ |
| | $-18 \leq k \leq 18$ | $-13 \leq k \leq 18$ | $-11 \leq k \leq 18$ | $-17 \leq k \leq 16$ |
| | $-24 \leq l \leq 21$ | $-23 \leq l \leq 20$ | $-24 \leq l \leq 24$ | $-15 \leq l \leq 25$ |
| reflections collected | 26602 | 19236 | 28284 | 20370 |
| unique reflections [$R_{int}$] | 14489 [0.0235] | 13968 [0.0441] | 14469 [0.0329] | 13442 [0.0569] |
| completeness to $\theta$ | 99.4% (25.50°) | 96.8% (25.50°) | 99.7% (25.50°) | 97.0% (25.03°) |
| data/restraints/parameters | 14489/6/1074 | 13968/5/1058 | 14469/0/1101 | 13442/91/932 |
| GOOF on $F^2$ | 1.062 | 1.025 | 1.023 | 1.064 |
| final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0332$, $wR_2 = 0.0752$ | $R_1 = 0.0531$, $wR_2 = 0.1205$ | $R_1 = 0.0321$, $wR_2 = 0.0681$ | $R_1 = 0.1280$, $wR_2 = 0.3489$ |
| $R$ indices (all data) | $R_1 = 0.0438$, $wR_2 = 0.0802$ | $R_1 = 0.0874$, $wR_2 = 0.1375$ | $R_1 = 0.0507$, $wR_2 = 0.0747$ | $R_1 = 0.1475$, $wR_2 = 0.3584$ |
| largest residual peaks (e Å$^{-3}$) | 2.196 and −1.415 | 2.210 and −1.450 | 1.548 and −1.279 | 5.025 and −2.818 |

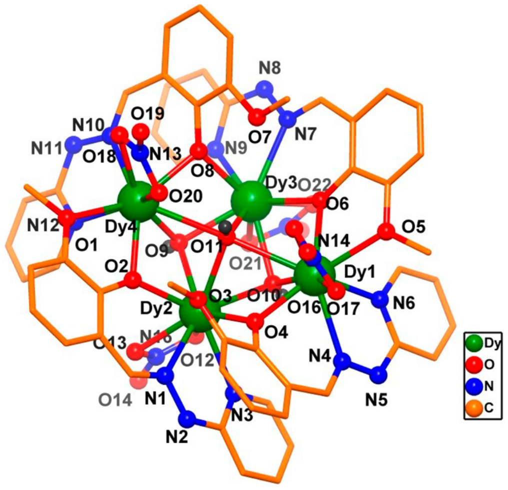


**Figure 1.** Molecular structure of **3**. All hydrogen atoms have been omitted for clarity.

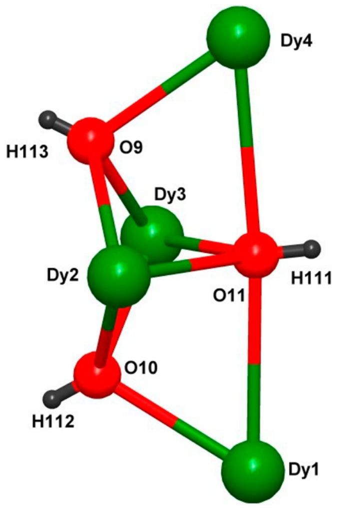


**Figure 2.** Seesaw geometry of the $Dy_4$ core of **3**. Notice the capping hydroxide ligands on two faces of the structure.

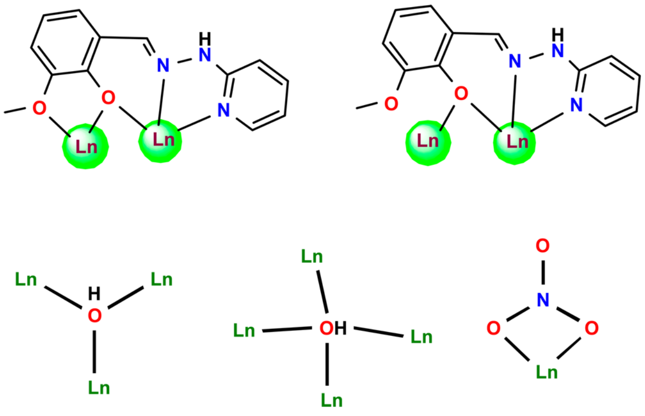
were analyzed by full-matrix diagonalization of the spin Hamiltonian described in eq 1 using MAGPACK.[27]

$$H = -2J_1(S_1S_2 + S_1S_3 + S_2S_4 + S_3S_4) - 2J_2(S_1S_4 + S_2S_3) \quad (1)$$

We found that the overall coupling within the $Gd_4$ complex was antiferromagnetic and that the data could be nicely reproduced with $J = J_1 = J_2 = -0.09$ cm$^{-1}$ and $g = 2$ (see the solid lines in Figures 4 and 5). This small interaction causes spin-frustration within the molecule and a high density of low-lying spin states that are easily accessible under applied magnetic fields-even at base temperature. Indeed, the maximum value of $M$ at 2 K and 7 T is 28.1 N$\mu_{B,}$ which is close to the expected value of 28 N$\mu_B$ for the four Gd(III) centers in **1**.

For the isostructural $Tb_4$, $Dy_4$, and $Ho_4$ analogues, $M$(H) at 2 K reaches values of 21.5, 21.6, and 22.4 N$\mu_B$, respectively, under an applied field of 7 T but does not show any sign of saturation (Figure 5). In addition, the $M(H/T)$ data of **2**−**4** at temperatures of 2 K and 4 K (Supporting Information) do not

**Chart 1. Coordination Modes of All of the Ligands Used in the Present Study**



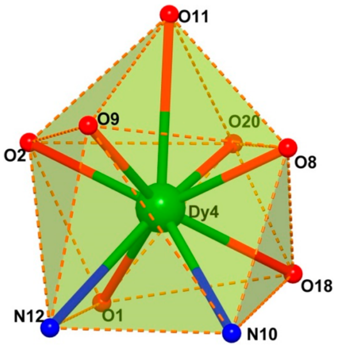


**Figure 3.** Nine coordinate distorted monocapped square antiprism geometry of the dysprosium center in **3**.

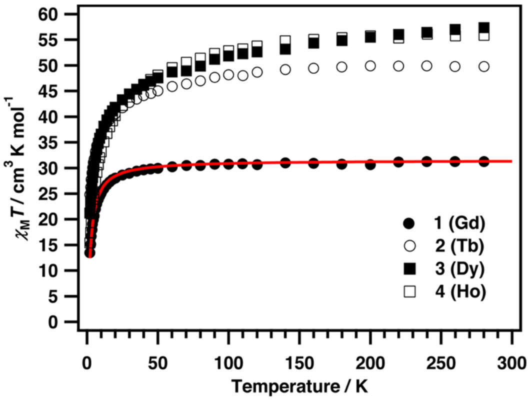


**Figure 4.** Temperature dependence of $\chi_M T$ for **1**−**4** at 0.1 T. The red line represents the best fit for **1** using eq 1 with the parameters $g$ = 2.00 and $J$ = −0.09 cm$^{-1}$.

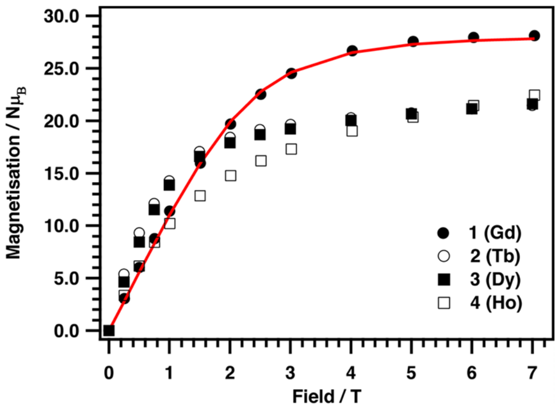


**Figure 5.** Field dependence of the magnetization for **1**−**4** recorded at 2 K. The red line is the best fit for **1** using eq 1 with the parameters $g$ = 2.00 and $J$ = −0.09 cm$^{-1}$.

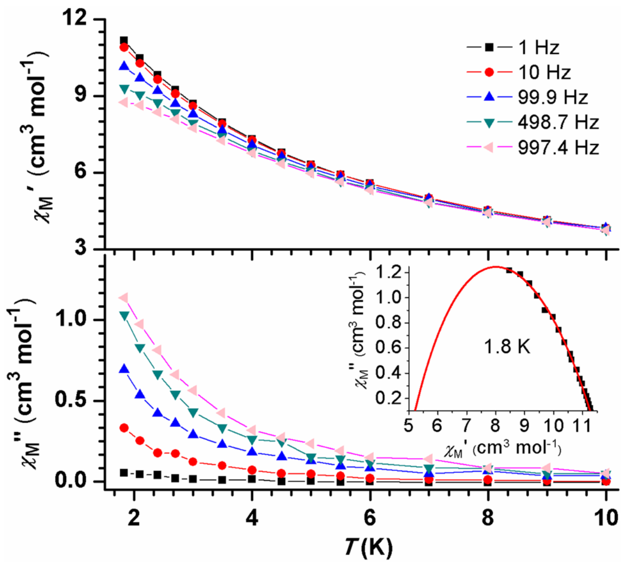


**Figure 6.** Temperature dependence of the ac magnetic susceptibility of **3** at five frequencies between 1 and 997 Hz. Inset: Cole−Cole plot for **3** at 1.8 K; the red line is a Debye fit at the data points yielding $\tau$ = 0.07 ms.

lie on a single master-curve, suggesting the existence of significant magnetic anisotropy and/or low-lying excited states.

The magnetization dynamics were investigated by alternating current (ac) susceptibility measurements as a function of temperature (1.8−10 K) and frequency ($\nu$ = 1−1400 Hz), at an ac field strength of 1.55 G and a dc field of either 0 or 1 kG. Among these complexes, only **3** shows clear evidence of slow magnetization relaxation. Below ca. 6 K, both the in-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) components of the ac susceptibility of **3** show strong frequency dependence, and an incomplete semicircular Cole−Cole plot is observed at 1.8 K (Figure 6). This indicates that a slow relaxation process takes place. The dynamics of this relaxation process cannot be properly assessed because of the lack of $\chi_M''(T, \nu)$ maxima above the temperature of 1.8 K, which is the lower limit of our commercial SQUID magnetometer. A Debye fit[28] applied to the isothermal $\chi_M''(\nu)$ data at 1.8 K yielded a relaxation time, $\tau$, of 0.07 ms (the inset of Figure 6).

## ■ CONCLUSION

In summary we have used a polydentate hydrazone Schiff base ligand to stabilize a tetranuclear Ln$_4$ cage (Ln = Gd(**1**), Tb(**2**), Dy(**3**), and Ho(**4**)) that exhibits a very unusual seesaw topology of its magnetic ions. To the best of our knowledge, this is the first tetranuclear lanthanide complex with such a structural motif.

Analysis of the magnetic data of the gadolinium analogue using an isotropic spin Hamiltonian has confirmed the presence of weak antiferromagnetic exchange within the tetrametallic core. The strength of this interaction was quantified by $J$ = −0.09 cm$^{-1}$. Ac magnetic susceptibility studies undertaken on the dysprosium analogue revealed a slow magnetic relaxation at low temperatures, which may be related to the single-ion crystal field effects associated with highly anisotropic Dy(III) ions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures and tabulated bond angles/lengths for the crystal structures of compounds **1**−**4**. Bond valence sum calculations for the oxygen atoms of compound **3**. Full results of the SHAPE analysis for the Ln(III) centers in **1**−**4** and for the tetrameric cores. Field-dependent magnetization for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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