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Hexanuclear 3d–4f Neutral $\text{Co}^{\text{II}}_2\text{Ln}^{\text{III}}_4$ Clusters: Synthesis, Structure, and Magnetism

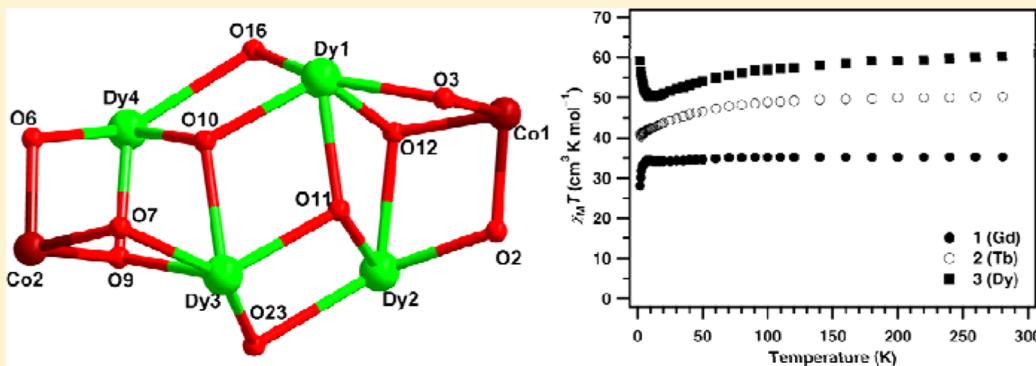
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Supporting Information



ABSTRACT: The sequential reaction of the multisite coordination ligand $6,6'-(2\text{-dimethylamino})\text{ethyl azanediyl}\text{bis}(\text{methylene})\text{bis}(2\text{-methoxy-4-methylphenol})$ (LH_2) with Ln^{III} salts ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$) and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of triethylamine and pivalic acid (pivH) in ambient conditions afforded a series of isostructural heterometallic hexanuclear $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes with the general formula $[\text{Co}^{\text{II}}_2\text{Ln}_4(\mu_3\text{-OH})_4(\text{L})_2(\text{piv})_8(\mu\text{-OH}_2)] \cdot w\text{CH}_3\text{C}\text{-xCH}_2\text{Cl}_2\text{-yCH}_3\text{OH}\text{-zH}_2\text{O}$ (1: $\text{Ln} = \text{Gd}$, $w = 5$, $x = 2$, $y = 0$, $z = 2$; 2: $\text{Ln} = \text{Tb}$, $w = 7$, $x = 4$, $y = 2$, $z = 0$; 3: $\text{Ln} = \text{Dy}$; $w = 4$, $x = 2$, $y = 2$, $z = 0$). Compounds 1 and 3 crystallize in the monoclinic system, space group $P2_1/n$ ($Z = 4$), while compound 2 crystallizes in $P2_1/n$ ($Z = 2$). The hexanuclear core of the complexes comprises of a nonplanar arrangement of lanthanide ions bridged by two $\mu_3\text{-OH}$ ligands. This tetranuclear motif is connected to the Co^{II} ions by two $\mu_3\text{-OH}$ ligands. The overall structure contains four interlinked incomplete cubic subunits (two $\text{Co}^{\text{II}}\text{Ln}^{\text{III}}_2\text{O}_4$ and two $\text{Ln}^{\text{III}}_3\text{O}_4$) that are connected to each other by the sharing of two Ln^{III} ions. The lanthanide centers are eight-coordinate (distorted trigonal-dodecahedron) and nine-coordinate (distorted monocapped square-antiprism), while the cobalt centers are six-coordinate (distorted octahedral). Magnetic measurement of the dysprosium analogue shows a slow magnetic relaxation.

INTRODUCTION

Research in the area of single-molecule magnets (SMMs) has been extremely prolific in recent years. The field started with the discovery of SMM behavior in $[\text{Mn}^{\text{IV}}_4\text{Mn}^{\text{III}}_8(\mu_3\text{-O})_{12}(\text{O}_2\text{C-Me})_{16}(\text{OH}_2)_4] \cdot 2\text{MeCO}_2\text{H} \cdot 4\text{H}_2\text{O}$ (Mn_{12} -acetate)¹ and has been growing ever since.^{2–9} The qualitative understanding that SMM behavior is observed in molecules that possess a large ground-state spin and a reasonable magnetic anisotropy^{2–11} has directed magneto chemists toward the design and assembly of homonuclear lanthanide complexes^{12–19} and heterometallic 3d/4f complexes, since these should be able to provide both properties at the same time.^{20–51} Although the initial paradigm in the 3d/4f system involved Cu^{II}/Ln^{III} complexes,⁵² a number of systems containing other transition metal ions are now being investigated.^{20–51}

Realizing that the inherent magnetic anisotropy of Co^{II} could be harnessed for the generation of spin clusters with an enhanced total anisotropy,^{20–24} we designed the phosphorus-supported ligand $\text{SP}(\text{N}(\text{Me})\text{N}=\text{CH-C}_6\text{H}_3\text{-2-OMe-3-OH})_3$, which allows the preparation of linear heterometallic [Co^{II}₂Ln]^{53,54} complexes, several of which have been shown to be SMMs.^{53,54} More recently, we prepared a Co^{II}/Co^{III} complex that also showed SMM behavior.⁵⁵ Spurred by these and other reports of Co^{II}-containing SMMs,^{56–58} we were interested in examining polynuclear Co^{II}/4f complexes.^{20–24,53,54,59–65}

One of the synthetic difficulties in this endeavor is the ready oxidation of Co^{II} to Co^{III} as encountered, for example, by Powell and co-workers in their report of a Co^{III}₂Ln^{III}₄ family.⁶⁶

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Table 1. Representative Examples of Heterometallic Co^{II}/Ln^{III} Complexes

nuclearity	complexes	property	topological nomenclature ²³	ref
Co/Ln (1:1)	[C ₉ H ₇ NH][Co ^{II} Tb ^{III} (Piv) ₃ (C ₉ H ₇ N)(NO ₃) ₃]·0.5H ₂ O	weak ferromagnetic interaction		79
Co/Ln (1:1)	[Co ^{II} Ln ^{III} (Piv) ₅ (C ₉ H ₇ N)(H ₂ O)]·0.5C ₉ H ₇ N (Ln = Gd, Dy)	weak ferromagnetic interaction		79
Co/Ln (1:1)	[LCo ^{II} (MeOH)Gd ^{III} (NO ₃) ₃][LCo ^{II} (AcO) ₂ Gd ^{III} (NO ₃) ₂] (H ₂ L = 1,3-bis[(3-methoxysalicylidene)amino]-2,2-dimethylpropane)	ferromagnetic interaction	1M2-1	80
Co ₂ Ln (2:1)	[Co ^{II} ₂ Gd ^{III} (Piv) ₆ (C ₉ H ₇ N) ₂ (NO ₃)]	weak ferromagnetic interaction		79
Co ₂ Ln (2:1)	[L ₂ Co ^{II} ₂ Gd ^{III}][NO ₃] ₂ CHCl ₃	SMM	1,2M3-1	53
Co ₂ Ln (2:1)	{(S)P[N(Me)N = CH-C ₆ H ₃ -2-O-3-OMe] ₃ } ₂ Co ^{II} Ln ^{III} ·NO ₃ (Ln = Tb, Gd, Dy)	SMM	1,2M3-1	54
Co ₂ Ln (2:1)	[LCo ^{II} Ln ^{III} Co ^{II} L]·NO ₃ (Ln = Dy, Tb, Gd, La)	SMM with large magnetization hysteresis loops	1,2M3-1	81
Co ₃ Ln (3:1)	[Co ^{II} ₃ Ln ^{III} (hmp) ₄ (OAc) ₅ (H ₂ O)] (Ln = Dy, Ho, Er, Tm, Yb, Y)	Ferromagnetic and Magnetocaloric effect (MCE)	3M4-1	24
Co ₄ Ln (4:1)	[Co ^{II} ₄ Ln ^{III} (L) ₄ (OAc) ₂ (S) ₄](NO ₃) (Ln = Dy, Tb, Gd, Ho)	antiferromagnetic interaction	2,4M5-1	61
Co ₆ Ln (6:1)	[Co ^{II} ₆ Gd ^{III} (aib) ₆ (OH) ₃ (NO ₃) _{2.9} (CH ₃ OH) _{4.9} (H ₂ O) _{1.2}] ₂ ·2.6(ClO ₄)·0.5(NO ₃) _{0.5} [Co ^{II} ₆ Dy ^{III} (aib) ₆ (OH) ₃ (NO ₃) _{2.9} (CH ₃ OH) _{4.92} (H ₂ O) _{1.18}](ClO ₄) _{2.6} (NO ₃) _{0.5} [Co ^{II} ₆ Ho ^{III} (aib) ₆ (OH) ₃ (NO ₃) ₃ (CH ₃ CN) ₆] ₂ ·0.27[Ho(NO ₃) ₃ (ClO ₄) _{0.35} (H ₂ O) _{0.15}] ₂ ·0.656[Co(NO ₃) ₃ (H ₂ O)] ₂ ·0.171(ClO ₄)	SMM	2,6M7-1	60
Co ₆ Ln (6:1)	[Co ^{II} ₆ Dy ^{III} (aib) ₆ (OH) ₃ (NO ₃) _{2.9} (CH ₃ OH) _{4.92} (H ₂ O) _{1.18}](ClO ₄) _{2.6} (NO ₃) _{0.5}	SMM		64
Co ₂ Ln ₂ (2:2)	[Co ^{II} ₂ Dy ^{II} ₂ (L) ₄ (NO ₃) ₂ (THF) ₂]	SMM	2,3M4-1	21
Co ₂ Ln ₂ (2:2)	[(pip)Co ^{II} L ₂ OMeGd ^{III} (CH ₃ COO)(hfa)] ₂ [CoL' ₂ Gd(thd) ₂ (MeOH)] ₂	antiferromagnetic and ferromagnetic interactions		59
Co ₂ Ln ₂ (2:2)	[(NO ₃) ₂ Gd ^{III} (ovan) ₂ (μ ₃ -HO)Co ^{II} ₂ (μ ₃ -OH)(ovan) ₂ Gd ^{III} (NO ₃) ₂] [(NO ₃) ₂ Tb ^{III} (ovan) ₂ (μ ₃ -HO)Co ^{II} ₂ (μ ₃ -OH)(ovan) ₂ Tb ^{III} (NO ₃) ₂]	SMM	2,3M4-1	22
Co ₂ Ln ₂ (2:2)	[Co ^{II} ₂ Ln ^{III} ₂ (pdMH) ₄ (Piv) ₆] (Ln = Dy, Tb, Gd)	SMM	3M4-1	23
Co ₄ Ln ₄ (4:4)	[Co ^{II} ₄ Ln ^{III} ₄ (OH) ₄ (chp) ₁₀ (acac) ₆] (Ln = Gd, Tb, Dy)	SMM	2,3,5M8-1	63
Co ₄ Ln ₁₀ (4:10)	[Co ^{II} ₄ Ln ^{III} ₁₀ (O ₂ CtBu) ₁₂ (O ₃ PC ₆ H ₁₀ NH ₂) ₈ (PO ₄) ₂ (O ₂ CMe) ₂ (O ₃ PC ₆ H ₁₀ NH ₃) ₂] (Ln = Gd, Dy)	MCE	1,2,3M7-1	5
Co ₄ Ln ₆ (4:6)	[Co ^{II} ₄ Gd ^{III} ₆ (O ₃ PCH ₂ Ph) ₆ (O ₂ CtBu) ₁₄ (MeCN) ₂]	MCE	2,3,4M10-1	65
Co ₈ Ln ₄ (8:4)	[Co ^{II} ₈ Gd ^{III} ₄ (O ₃ PtBu) ₆ (O ₂ CtBu) ₁₆]	MCE	2,3M12-1	65
Co ₈ Ln ₈ (8:8)	[Co ^{II} ₈ Gd ^{III} ₈ (μ ₃ -OH) ₄ (NO ₃) ₄ (O ₃ PtBu) ₈ (O ₂ CtBu) ₁₆]	MCE	2,3,4M16-1	65
Co ₈ Ln ₈ (8:8)	[Co ^{II} ₈ Ln ^{III} ₈ (μ ₃ -OH) ₄ (NO ₃) ₄ (O ₃ PtBu) ₈ (O ₂ CtBu) ₁₆] (Ln = Gd, Tb, Dy, Ho, Er, Yb, Y).	MCE	2,3,4M16-1	64

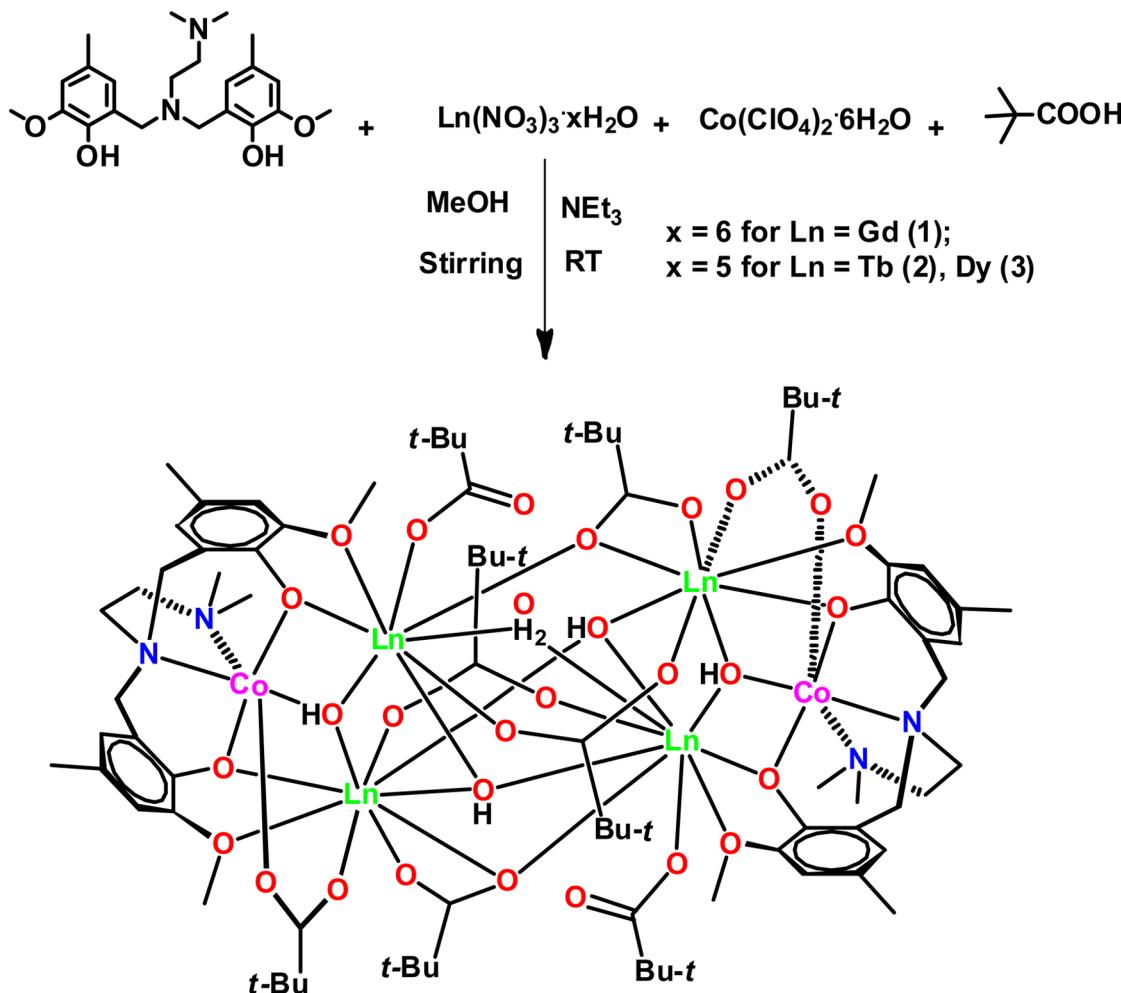
In this account we report the successful stabilization of Co^{II} in a similar hexanuclear framework using a multicomponent synthesis, generating the following compounds: [Co^{II}₂Ln₄(μ₃-OH)₄(L)₂(piv)₈(μ-OH₂)]_wCH₃CN_xCH₂Cl₂_yCH₃OH_zH₂O (**1**: Ln = Gd, w = 5, x = 2, y = 0, z = 2; **2**: Ln = Tb, w = 7, x = 4, y = 2, z = 0; **3**: Ln = Dy; w = 4, x = 2, y = 2, z = 0; LH₂ = 6,6'-{(2-(dimethylamino)ethyl azanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol); pivH = pivalic acid). The synthesis, structure, and magnetism of all three compounds are discussed.

EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.⁶⁷ The following chemicals were used as obtained: 2-methoxy-4-methyl phenol, N,N-dimethylethylenediamine, Gd(NO₃)₃·6H₂O, Tb(NO₃)₃·5H₂O, Dy(NO₃)₃·5H₂O, and Co(ClO₄)₂·6H₂O (Aldrich, USA), 37% formaldehyde solution and triethylamine (S. D. Fine Chemicals, India). The ligand 6,6'-{(2-(dimethylamino)ethyl azanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol) (LH₂) was prepared by modification of a literature method.^{69,86}

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a JEOL-JNM LAMBDA 400 model NMR spectrometer operating at 400.0 MHz in CDCl₃ solution. Chemical shifts are referenced with respect to tetramethylsilane. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400 to 4000 cm⁻¹. Elemental analyses of the compounds were obtained using a Thermoquest CE instrument CHNS-O, EA/110 model. ESI-MS spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 Advanced powder diffractometer with CuK_α radiation. 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

Scheme 1. Synthesis of Complexes 1–3



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 1–3 were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using graphite-monochromated MoK α radiation ($\lambda_{\alpha} = 0.71073 \text{ \AA}$). The crystals did not degrade/decompose during data collection. Data collection, structure solution, and refinement were performed using SMART, SAINT, and SHELXTL programs, respectively.^{70–78} All calculations for the data reduction were done using the Bruker SADABS program. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares procedures, while the hydrogen atoms were fixed to idealized positions and used a riding model. Several solvent accessible voids remain in all the structures, and these are presumably filled with several disordered dichloromethane, acetonitrile, methanol, and water molecules. Modeling of these solvents proved futile with the quality of the current data, and therefore the PLATON/SQUEEZE^{76–78} program was used to remove the heavily disordered solvent molecules. The total electron count removed per unit cell by SQUEEZE was 1: 853; 2: 719; 3: 824. This corresponds to the following number of electrons per molecule: 1: 213; 2: 359; 3: 206 ($Z = 4$ for complexes 1 and 3 and $Z = 2$ for complex 2). These were assigned to the following solvent molecules: 1: 5CH₃CN, 2CH₂Cl₂, and 2H₂O; 2: 7CH₃CN, 4CH₂Cl₂, and

2CH₃OH; 3: 4CH₃CN, 2CH₂Cl₂, and 2CH₃OH. All of the mean plane analyses and molecular drawings were obtained using DIAMOND (version 3.1).

Syntheses. Preparation of 1–3. The following general protocol was applied for the preparation of all three compounds. A methanolic solution (5 mL) of Ln(No₃)₃·xH₂O (3 equiv) was added dropwise to a 20 mL methanolic solution of a mixture of 6,6'-(2-(dimethylamino)ethyl azanediyl)bis(methylene)bis(2-methoxy-4-methylphenol) (LH₂) (2 equiv) and triethylamine (8 equiv) with constant stirring. To this reaction mixture, solid Co(ClO₄)₂·6H₂O (3 equiv) was added, and the mixture was left stirring for 1.5 h. A deep pink-colored solution was obtained. Pivalic acid (4 equiv) was added and the stirring was continued for 12 h. The resulting pink solution was dried fully *in vacuo*, resulting in a solid residue. This was redissolved in an acetonitrile/dichloromethane (1:1) mixture and filtered. The filtrate was left to crystallize under slow evaporation at room temperature. After 1 week, brown block-shaped crystals suitable for X-ray analysis were obtained. The quantities of the reactants used in each reaction and the characterization data of the compounds are given below.

Caution! Reactions of perchlorate metal salts with organic ligands are potentially explosive. A small amount of perchlorate salt should be used, and it should be handled with care.

[Co^{II}₂Gd₄(μ₃-OH)₄(L)₂(piv)₈(μ-OH)₂]·5CH₃CN·2CH₂Cl₂·2H₂O (1). Co(ClO₄)₂·6H₂O (0.062 g, 0.169 mmol), Gd(No₃)₃·6H₂O (0.077 mg, 0.170 mmol), LH₂(0.044 g, 0.113 mmol), Et₃N (0.046 g, 0.454

mmol), and pivalic acid (0.023 g, 0.225 mmol). Yield: 0.062 g, 51% (based on Gd). Mp: >230 °C. IR (KBr, ν/cm^{-1}): 3447(br), 2956(s), 2923(m), 2866(m), 1562(s), 1496(s), 1463(s), 1418(s), 1373(s), 1359(s), 1300(s), 1266(s), 1251(s), 1228(s), 1154(s), 1079(s), 1033(m), 934(w), 828(s), 783(w), 623(m), 597(s), 462(s). Anal. Calcd for $C_{98}H_{164}Cl_4Gd_4N_{10}Co_2O_{31}$ (2867.07): C, 41.05; H, 5.77; N, 4.89; Found: C, 40.76; H, 5.56; N, 4.66. ESI-MS (m/z): 1021.5865, $[(\text{L})_2\text{Co}_2\text{Gd}_4(\text{OH})_7(\text{O}_2\text{CCMe}_3)_3 + \text{H}_2\text{O} + 2\text{CH}_3\text{CN}]^{2+}$.

$[\text{Co}^{\text{II}}_2\text{Tb}_4(\mu_3\text{-OH})_4(\text{L})_2(\text{piv})_8(\mu\text{-OH}_2)_2\text{J}\cdot7\text{CH}_3\text{CN}\cdot4\text{CH}_2\text{Cl}_2\cdot2\text{CH}_3\text{OH}$ (2). $\text{Co}(\text{ClO}_4)_2\cdot6\text{H}_2\text{O}$ (0.062 g, 0.169 mmol), $\text{Tb}(\text{NO}_3)_3\cdot5\text{H}_2\text{O}$ (0.074 mg, 0.170 mmol), LH_2 (0.044 g, 0.113 mmol), Et_3N (0.046 g, 0.454 mmol), and pivalic acid (0.023 g, 0.223 mmol). Yield: 0.074 g, 54% (based on Tb). Mp: >230 °C. IR (KBr, ν/cm^{-1}): 3594 (br), 2957(s), 2924(s), 2868(m), 1684(w), 1560(s), 1498(s) 1482(s), 1463(s), 1420(s), 1371(s), 1299(m), 1229(s), 1154(s), 1088(s), 1069(w), 1028(w), 972(m), 951(s), 904(s), 828(s), 783(m), 626(w), 597(s), 466(s). Anal. Calcd for $C_{104}H_{175}\text{Cl}_8\text{Tb}_4\text{N}_{11}\text{Co}_2\text{O}_{31}$ (3112.74): C, 40.13; H, 5.67; N, 4.95; Found: C, 39.86; H, 5.44; N, 4.75. ESI-MS (m/z): 848.3591, $[(\text{L})_2\text{Co}_2\text{Tb}_2(\text{OH})_5]^{+}$.

$[\text{Co}^{\text{II}}_2\text{Dy}_4(\mu_3\text{-OH})_4(\text{L})_2(\text{piv})_8(\mu\text{-OH}_2)_2\text{J}\cdot4\text{CH}_3\text{CN}\cdot2\text{CH}_2\text{Cl}_2\cdot2\text{CH}_3\text{OH}$ (3). $\text{Co}(\text{ClO}_4)_2\cdot6\text{H}_2\text{O}$ (0.062 g, 0.169 mmol), $\text{Dy}(\text{NO}_3)_3\cdot5\text{H}_2\text{O}$ (0.074 mg, 0.169 mmol), LH_2 (0.044 g, 0.113 mmol), Et_3N (0.046 g, 0.454 mmol), and pivalic acid (0.023 g, 0.223 mmol). Yield: 0.069 g, 57% (based on Dy). Mp: >230 °C. IR (KBr, ν/cm^{-1}): 3444 (br), 2956 (s), 2924(m), 2866(m), 1562(s), 1483(s), 1463 (s), 1419 (s), 1372(s), 1359(s), 1299(m), 1251(s), 1229(s), 1154(s), 1079(s), 1032(m), 934(m), 829(s), 783(w), 628(w), 597(s), 467(w). Anal. Calcd for $C_{96}H_{162}\text{Cl}_4\text{Dy}_4\text{N}_8\text{Co}_2\text{O}_{31}$ (2834.02): C, 40.69; H, 5.76; N, 3.95; Found: C, 40.36; H, 5.52; N, 3.76. ESI-MS (m/z): 1021.1149, $[(\text{L})_2\text{Co}_2\text{Dy}_4(\text{OH})_8(\text{O}_2\text{CCMe}_3)_2 + 4\text{CH}_3\text{CN}]^{2+}$.

RESULTS AND DISCUSSION

Synthetic Aspects. A literature search on heterometallic $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes reveals that in this family varying

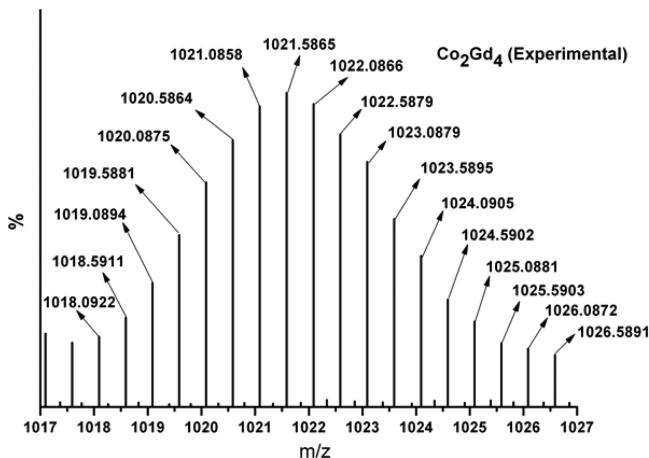


Figure 1. ESI-MS of 1 (experimental).

nuclearities and ratios of $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ are present. Representative examples of di-^{79,80} and trinuclear^{53,54,79–81} derivatives are shown in Figure S1, Supporting Information. Table 1 gives a summary of the representative examples of heterometallic $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes and their topological nomenclature.⁸² The current hexanuclear family represents the *first example* of its kind containing Co^{II} and is only the fourth example of a hexanuclear family possessing any combination of a 3d and a 4f ion. The other three previously known compounds are $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_4(\mu_4\text{-O})_2(\text{hmp})_4(\text{pic})_2(\text{piv})_6(\mu\text{-N}_3)_2]$ (Hhmp = 2-(hydroxymethyl) pyridine; Hpiv = pivalic acid, picH = 2-picolinic acid),⁸³ $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_4\text{L}_2(\mu_4\text{-O})_2(\text{N}_3)_2(\text{CH}_3\text{O})_2$ -

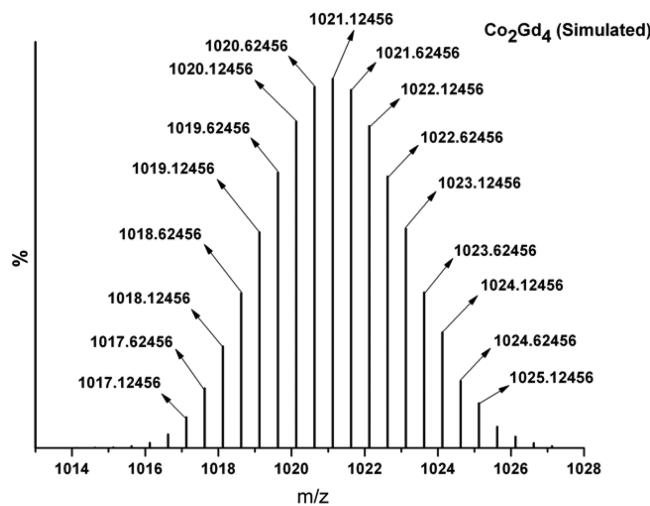


Figure 2. ESI-MS of 1 (simulated).

$(\text{CH}_3\text{OH})_4(\text{NO}_3)_2]$ ($\text{H}_4\text{L} = N,N'\text{-dihydroxyethyl-}N,N'\text{-(2-hydroxy-4,5-dimethylbenzyl)ethylenediamine}$),⁸⁴ and $(\text{pipzH}_2)\cdot[\text{Cr}^{\text{III}}_2\text{Dy}^{\text{III}}_4(\mu_4\text{-O})_2(\mu_3\text{-OH})_4(\text{H}_2\text{O})_{10}(\mu_3\text{-SO}_4)_4(\text{SO}_4)_2]$ (pipzH = piperazine).⁸⁵ These compounds are shown in Figure S2. A recent example of the squashed $\text{Fe}^{\text{III}}_2\text{Dy}^{\text{III}}_4$ octahedra complex was synthesized by Polyzou et al. (Figure S3).⁸⁶ In this structure, the four Ln^{III} ions are also a planar rectangular arrangement.

We have previously utilized the multitopic ligand LH_2 in conjunction with pivalic acid to prepare a series of Ni_3Ln_3 hexanuclear derivatives.⁸⁷ Using a similar strategy, the reaction of LH_2 with $\text{Co}(\text{ClO}_4)_2\cdot6\text{H}_2\text{O}$, $\text{Ln}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$, NEt_3 , and pivalic acid in a 2:3:3:8:4 stoichiometric ratio afforded the neutral heterometallic hexanuclear complexes in the present study (Scheme 1). Compounds 1 and 3 retain their molecular integrity in solution as revealed by the presence of m/z peaks corresponding to the mass of the parent ion (1: 1021.5865, Figures 1 and 2; 2: 1021.1149, Figures S4–S5), while compound 2 appears to fragment, with a maximum m/z peak (848.3591) that is significantly lower than the expected mass of the parent ion (Figures S6–S7).

Molecular Structures of 1–4. The molecular structures of 1–3 were determined by single-crystal X-ray crystallography. 1 and 3 crystallize in the monoclinic system with $P2_1/n$ ($Z = 4$), while 2 crystallizes in the space group $P2/n$ ($Z = 2$). The asymmetric unit of 2 contains half of the total molecule, whereas the asymmetric units of 1 and 3 contain the full molecule. The crystallographic parameters of these compounds are given in Table 2. In view of the structural similarities of these compounds, the molecular structure of 3 is described as a representative example. The structural details of all the other compounds are given in the Supporting Information. The various coordination modes of all the ligands found in 1–3 are summarized in Figure S8.

The molecular structure of 3 is shown in Scheme 1 and Figure 3. Compound 3 is a neutral heterometallic hexanuclear derivative possessing a nonplanar Dy_4 subcore derivative (Figures 4–5). It is interesting to compare the hexanuclear core of the current members with those reported in the literature. Thus, in the aforementioned manganese derivatives, $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_4(\mu_4\text{-O})_2(\text{hmp})_4(\text{pic})_2(\text{piv})_6(\mu\text{-N}_3)_2]$ ⁸³ and $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_4\text{L}_2(\mu_4\text{-O})_2(\text{N}_3)_2(\text{CH}_3\text{O})_2(\text{CH}_3\text{OH})_4(\text{NO}_3)_2]$,⁸⁴ the central Ln_4 is planar, while in the Cr_2Ln_4 derivative,

Table 2. Crystal Data and Structure Refinement Parameters of 1–3

compound	1	2	3
formula	C ₈₆ H ₁₃₉ Co ₂ Gd ₄ N ₅ O ₂₉	C ₈₄ H ₁₃₈ Co ₂ Tb ₄ N ₄ O ₂₉	C ₈₄ H ₁₃₈ Co ₂ Dy ₄ N ₄ O ₂₉
formula weight	2453.89	2421.57	2435.85
temp (K)	100(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2/n	P2 ₁ /n
unit cell dimensions, <i>a</i> (Å)	15.794(5)	15.791(5)	15.711(5)
<i>b</i> (Å)	41.582(5)	21.888(5)	41.655(5)
<i>c</i> (Å)	17.323(5)	17.177(5)	17.212(5)
α (deg)	90	90	90
β (deg)	101.674(5)	99.201(5)	100.778(5)
γ (deg)	90	90	90
volume (Å ³); <i>Z</i>	11141(5); 4	5861(3); 2	11066(5); 4
density (Mg m ⁻³)	1.463	1.372	1.462
abs. coef. (mm ⁻¹)	2.705	2.719	3.025
<i>F</i> (000)	4928	2432	4880
crystal size (mm)	0.16 × 0.14 × 0.12	0.16 × 0.14 × 0.12	0.16 × 0.14 × 0.12
θ range (deg)	0.98–25.50	4.08–25.03	2.18–25.50
limiting indices	$-19 \leq h \leq 18$ $-45 \leq k \leq 50$ $-17 \leq l \leq 20$	$-18 \leq h \leq 18$ $-17 \leq k \leq 26$ $-20 \leq l \leq 19$	$-16 \leq h \leq 19$ $-48 \leq k \leq 50$ $-20 \leq l \leq 20$
reflections collected	59498	29817	72387
unique reflections [<i>R</i> _{int}]	20633 [0.0671]	10320 [0.0743]	20581 [0.0524]
completeness to θ	99.5% (25.50°)	99.5% (25.03°)	99.9% (25.50°)
data/restraints/parameters	20633/98/1164	10320/15/585	20581/122/1156
GOF on <i>F</i> ²	1.089	0.906	1.076
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0715 <i>wR</i> ₂ = 0.1987	<i>R</i> ₁ = 0.0490 <i>wR</i> ₂ = 0.1054	<i>R</i> ₁ = 0.0839 <i>wR</i> ₂ = 0.1764
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0932 <i>wR</i> ₂ = 0.2232	<i>R</i> ₁ = 0.0789 <i>wR</i> ₂ = 0.1174	<i>R</i> ₁ = 0.1058 <i>wR</i> ₂ = 0.1838
largest residual peaks (e·Å ⁻³)	4.800 and -1.836	1.010 and -0.828	4.508 and -4.950

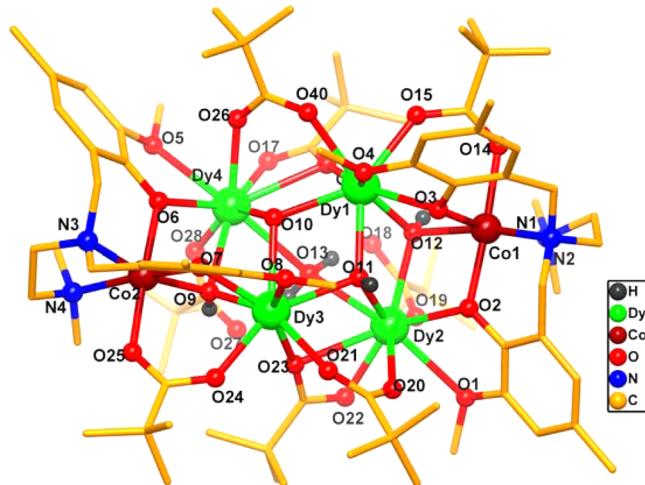


Figure 3. Molecular structure of 3. All the hydrogen atoms have been omitted for clarity.

(pipzH₂)₂[Cr^{III}₂Dy^{III}₄(μ_4 -O)₂(μ_3 -OH)₄(H₂O)₁₀(μ_3 -SO₄)₄(SO₄)₂]⁸⁵⁻, the central Ln₄ is planar, with the two Cr^{III} ions present on the top and bottom of this plane (Figure S2). Similarly, in the Co^{III}₂Ln^{III}₄ compound, [Co^{III}₂Ln^{III}₄(μ_3 -OH)₂(hmp)₄(μ -N₃)₂(piv)₈(NO₃)₂]⁶⁶⁻, the Ln₄ core is again planar (Scheme S1).

The core structure of compound 3 has a central tetranuclear nonplanar Dy^{III}₄ array that is connected to two Co^{II} ions on either side through the bridging action of [μ_3 -OH]⁻ ligands.

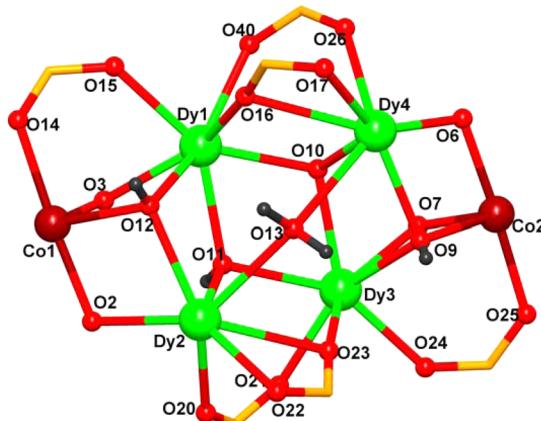


Figure 4. Core structure of compound 3.

The oxidation states of the Co^{II} and hydroxide ligands were assigned by the requirements of charge balance and bond valence sum (BVS) analysis (Tables S1–2).^{88–91}

The hexanuclear ensemble in 3 is made possible by the cumulative coordination action of [L]²⁻, [OH]⁻, and [tBuCO₂]⁻, the coordination modes of all of which are summarized in Figure S8. Each [L]²⁻ holds a trinuclear Dy–Co–Dy motif together, the methoxy groups bind to Dy ions, and the phenolate bridges Co^{II} and Dy^{III} ions. The two nitrogen centers of [L]²⁻ bind exclusively to the Co^{II} center.

Two [OH]⁻ ligands function in a μ_3 manner by bridging one Co^{II} and two Dy^{III} ions (Figure 3). On the other hand, two

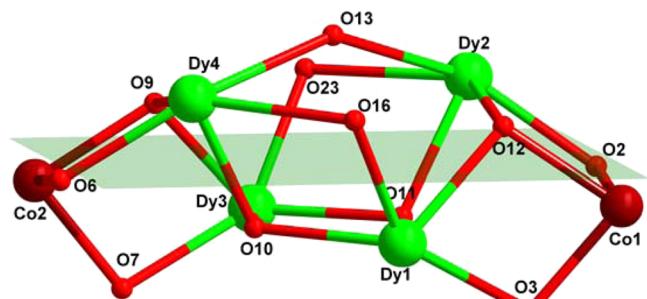


Figure 5. Mean plane of compound 3.

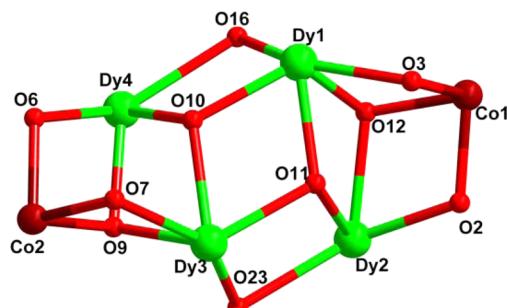


Figure 6. Incomplete cubic structural motifs present in 3.

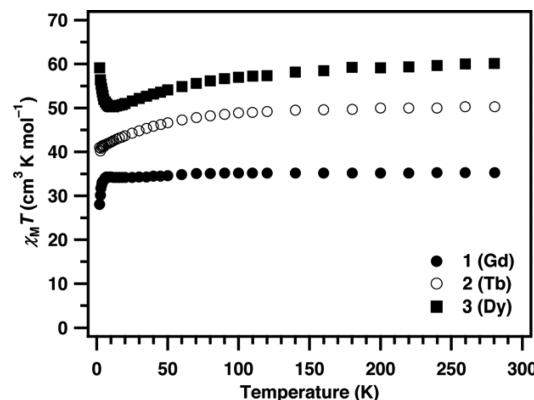


Figure 8. Temperature-dependent molar magnetic susceptibility for 1–3 at 0.1 T.

other $[\text{OH}]^-$ ligands also function in a μ_3 manner, but bind to three Dy^{III} ions (Figure 3). Interestingly, a pair of Dy^{III} ions (Dy2 and Dy4) are bridged by a neutral water molecule (Figure 3). Further, Dy1 is connected to Dy4 by two syn-syn bridged pivalate ligands. Another pivalate ligand is involved in a bridging coordination action to bind Dy1 and Co1 ions. Finally, Dy2 and Dy4 also possess, η^1 -coordinated pivalate ligands.

Mean plane analysis of 3 reveals that the two Dy^{III} ions (Dy1 and Dy2) are below the mean plane of the hexanuclear core

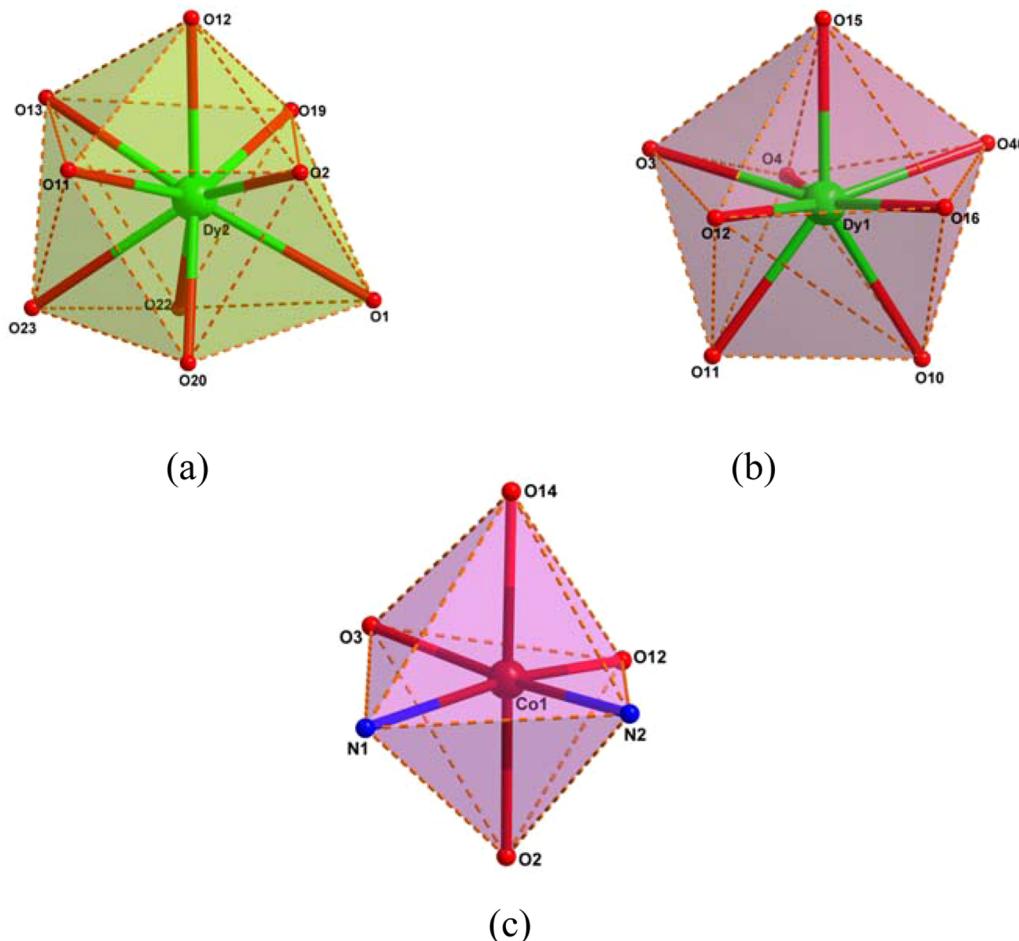


Figure 7. Coordination geometry around the metal center (a) Dy2 center distorted mono capped square-antiprism, (b) Dy1 center distorted trigonal-dodecahedron, and (c) Co1 center distorted octahedron geometry in compound 3.

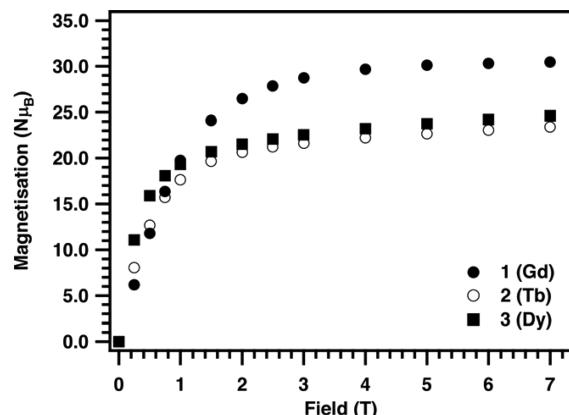


Figure 9. Field-dependent magnetization for **1–3** at 2 K.

(passing through the two Co^{II} ions), while the other two Dy^{III} ions (Dy2 and Dy4) are above the plane (Figure 5). Similarly, two μ_3 -OH ligands (O10, O11) are below the plane, while the other two μ_3 -OH units (O9, O12) are above the plane (Figure 5). Another interesting feature is that the water molecule bridges the two Dy^{III} ions (Dy2 and Dy4), which are also present above the plane (Figure 5). A structural examination of the core of **3** reveals the presence of four incomplete cubic subunits with one missing vertex (two Dy₂Co₄ and two Dy₃O₄) (Figure 6). The two incomplete subunits are connected to each other by the sharing of two common dysprosium ions (Figure 6).

Finally, as a result of the coordination of various ligands as described above, two types of Dy^{III} ions are found: Dy1 (eight-coordinate, DyO₈, distorted trigonal-dodecahedron) and Dy2 (nine-coordinate, DyO₉, distorted mono capped square-antiprism) (Figure 7). On the other hand, only one type of Co^{II} is found (six-coordinate, O₄N₂, distorted octahedral) (Figure 7). The hexametallic ensemble possesses several metal-containing rings, the sizes of which vary from 4 to 12 (Supporting Information). Interestingly compound **1** contains several supramolecular C–H– π , C–H–N, and C–H–O interactions (Supporting Information). The CH– π , CH–N, and CH–O interactions are moderately strong. The corresponding bond parameters are 2.447 Å, 2.651(2) Å, and 2.703(6) Å. We have checked the phase purity of all the three complexes (**1–3**) using powder X-ray diffraction analysis (Supporting Information), which show good agreement with the simulated patterns.

Magnetic Studies. The temperature dependence of the molar magnetic susceptibility, χ_M , was investigated for all three compounds under an applied magnetic field of 0.1 T, and the results are given as $\chi_M T$ versus T in Figure 8. The observed room temperature values of $\chi_M T$ for compounds **1–3** are 35.0, 50.0, and 59.7 cm³ K mol⁻¹, respectively. These values are a sum of contributions from both the Ln^{III} and Co^{II} ions in an uncoupled regime. We can calculate the expected contribution to the room temperature moment from the three Ln^{III} ions (**1**: 31.5; **2**: 47.3; **3**: 56.7 cm³ K mol⁻¹) using the following values: Gd^{III} (⁸S_{7/2}, $S = 7/2$, $L = 0$, $g = 2$, $C = 7.88$ cm³ K mol⁻¹), Tb^{III} (⁷F₆, $S = 3$, $L = 3$, $g = 3/2$, $C = 11.82$ cm³ K mol⁻¹), and Dy^{III} (⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17$ cm³ K mol⁻¹). However, calculation of the contribution from the Co^{II} ions is not as straightforward. In all cases the observed $\chi_M T$ values appear to be higher than those expected in the spin-only case: Co^{II} ($S = 3/2$, $L = 0$, $g = 2$, $C = 1.875$ cm³ K mol⁻¹), which is

consistent with Co^{II} in an octahedral environment, wherein a significant first order orbital contribution is expected.

For compounds **1–3**, $M(H)$ at 2 K reaches values of 30.5, 23.4, and 24.6 N_μB, at a 7 T applied field, respectively, failing to reach saturation in all cases (Figure 9). In addition, the $M(H/T)$ data of **1–3** at temperatures of 2 and 4 K (Supporting Information) do not lie on a single master-curve, suggesting the existence of significant magnetic anisotropy and/or low-lying excited states.

Alternating current (ac) susceptibility measurements were used to assess the magnetization dynamics 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 under a static dc field of either 0 or 0.1 T. Among these complexes, only **3** shows clear evidence of slow magnetization relaxation, and only under the applied field. Below ca. 7 K at a static field of 0.1 T, both the in-phase (χ_M') and out-of-phase (χ_M'') components of the ac susceptibility of **3** show a small but significant frequency dependence (Supporting Information).

CONCLUSION

In summary, a mixed-metal Co^{II}/Ln^{III} cage was prepared using the noncompartmental ligand 6,6-{(2-(dimethylamino)ethyl azanediyl)bis(methylene)} bis(2-methoxy-4-methylphenol) (LH₂) along with pivalic acid in the presence of triethylamine, thus demonstrating the utility of the Mannich base ligand in the assembly of heterometallic clusters. Magnetic measurements are consistent with the proposed formulations and reveal a slow magnetic relaxation in the dysprosium analogue. We are currently working on the modulation of this ligand in both homo- and heterometallic systems.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information files (CIF), scheme and additional figures, tables of bond distance (Å) and bond angle (deg) and BVS calculation table. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00588.

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Notes

The authors declare no competing financial interest.

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