Inorganic Chemistry
Article
pubs.acs.org/IC

Hexanuclear, Heterometallic, Ni_3Ln_3 Complexes Possessing O-Capped Homo- and Heterometallic Structural Subunits: SMM Behavior of the Dysprosium Analogue

Joydeb Goura,[†] Rogez Guillaume,[‡] Eric Rivière,[§] and Vadapalli Chandrasekhar*,[†,∥]

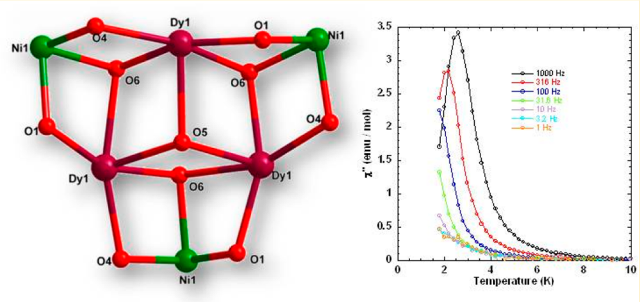
[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

[‡]Institut de Physique et Chimie des Matériaux de Strasbourg and Labex NIE, University of Strasbourg, CNRS UMR 7504, 67034 Strasbourg Cedex 2, France

[§]Equipe de Chimie Inorganique, ICMMO (CNRS, UMR 8182, Université Paris-Sud), Orsay F-91405, France

[∥]National Institute of Science Education and Research, Institute of Physics Campus, Sachivalaya Marg, Sainik School, Bhubaneswar, Orissa 751 005, India

Ⓢ *Supporting Information*



ABSTRACT: The reaction of hetero donor chelating mannich base ligand 6,6′-{(2-(dimethylamino)ethylazanediyl)-bis(methylene)}bis(2-methoxy-4-methylphenol) with $Ni(ClO_4)_2 \cdot 6H_2O$ and lanthanide(III) salts [Dy(III) (**1**); Tb(III) (**2**); Gd (III) (**3**); Ho(III) (**4**); and Er(III) (**5**)] in the presence of triethylamine and pivalic acid afforded a series of heterometallic hexanuclear Ni(II)−Ln(III) coordination compounds, $[Ni_3Ln_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3] \cdot (ClO_4) \cdot wCH_3CN \cdot xCH_2Cl_2 \cdot yCH_3OH \cdot zH_2O$ [for **1**, $w = 8$, $x = 3$, $y = 0$, $z = 5.5$; for **2**, $w = 0$, $x = 5$, $y = 0$, $z = 6.5$; for **3**, $w = 15$, $x = 18$, $y = 3$, $z = 7.5$; for **4**, $w = 15$, $x = 20$, $y = 6$, $z = 9.5$; and for **5**, $w = 0$, $x = 3$, $y = 2$, $z = 3$]. The molecular structure of these complexes reveals the presence of a monocationic hexanuclear derivative containing one perchlorate counteranion. The asymmetric unit of each of the hexanuclear derivatives comprises the dinuclear motif $[NiLn(L)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu\text{-}Piv)]$. The cation contains three interlinked O-capped clusters: one $Ln^{III}{}_3O$ and three $Ni^{II}Ln^{III}{}_2O$. Each of the lanthanide centers is eight-coordinated (distorted trigonal-dodecahedron), while the nickel centers are hexacoordinate (distorted octahedral). The study of the magnetic properties of all compounds are reported and suggests single molecule magnet behavior for the Dy(III) derivative (**1**).

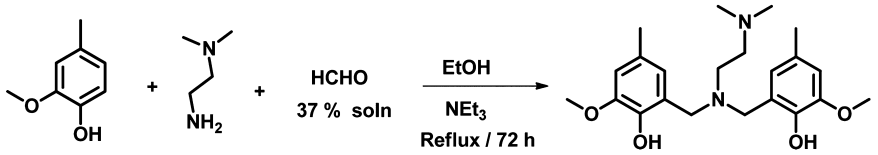
■ INTRODUCTION

Since the discovery of the first single-molecule magnet (SMM), $[Mn^{IV}{}_4Mn^{III}{}_8(\mu_3\text{-}O)_{12}(O_2C\text{-}Me)_{16}(OH_2)_4] \cdot 2MeCO_2H \cdot 4H_2O$,[1] there has been considerable attention in this area. Several efforts by synthetic chemists to assemble polynuclear transition metal ion complexes have been motivated by this discovery with an aim to achieve a high ground-state spin (S).[2] The realization that uniaxial magnetic anisotropy (D) is equally important led to efforts to incorporate metal ions that would show this property as a result of a structural distortion (such as Jahn−Teller distortion for a Mn(III) in an octahedral geometry)[3] or a spin−orbit coupling (such as Co(II)).[4] A second paradigm in this area is reflected by an investigation in the field of heterometallic 3d/4f complexes where two factors, viz., S and D, can be optimized by taking advantage of the large inherent anisotropy of certain lanthanide ions.[5] Since the first example, viz., a Cu−Gd complex,[6] many 3d/4f heterometallic complexes with varying nuclearities, transition metals, and transition metal/lanthanide ion ratios have been prepared and investigated with mixed success.[7−14] Among such compounds, those containing Co/Ln, Mn/Ln, and Ni/Ln compounds are of interest because Ni(II) can contribute to magnetic anisotropy.[7] From our lab, by using phosphorus-supported hydrazone ligands, we have investigated new families of Co_2Ln,[15] Mn_2Ln,[16] CuLn,[17] and Ni_2Ln[18] complexes, many of which have been shown to be SMMs. Encouraged by these results and considering the relative paucity of heterometallic 3d/4f complexes containing Ni(II), we examined the possibility of assembling polynuclear heterometallic complexes containing Ni(II) and lanthanide metal ions. One of the key ingredients for success in this area is the design of ligands that allow specific binding of both transition metal and lanthanide metal ions at the same time, allowing magnetic interactions between them through an appropriate single-atom or multiatom bridges. Another requirement is that the ligand through a multifunctional property should allow assembly of polynuclear complexes. Keeping these requirements in mind we prepared

Received: December 18, 2013
Published: July 22, 2014

dx.doi.org/10.1021/ic403090z | *Inorg. Chem.* 2014, 53, 7815−7823

Scheme 1. Synthesis of Ligand LH_2



the multidentate ligand 6,6′-{(2-(dimethylamino)ethylazanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol) and using it along with a coligand, pivalic acid, assembled a new family of hexanuclear heterometallic complexes, $[Ni_3Ln_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot wCH_3CN\cdot xCH_2Cl_2\cdot yCH_3OH\cdot zH_2O$ [for **1**, $w = 8$, $x = 3$, $y = 0$, $z = 5.5$; for **2**, $w = 0$, $x = 5$, $y = 0$, $z = 6.5$; for **3**, $w = 15$, $x = 18$, $y = 3$, $z = 7.5$; for **4**, $w = 15$, $x = 20$, $y = 6$, $z = 9.5$; and for **5**, $w = 0$, $x = 3$, $y = 2$, $z = 3$]. The synthesis, structure, and magnetism of these complexes are discussed herein.

■ EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.[19] The following chemicals were used as obtained: 2-methoxy-4-methyl phenol, *N*,*N*-dimethylethylenediamine, $Gd(NO_3)_3\cdot 6H_2O$, $Tb(NO_3)_3\cdot 5H_2O$, $Dy(NO_3)_3\cdot 5H_2O$, $Ho(NO_3)_3\cdot 5H_2O$, and $Er(NO_3)_3\cdot 5H_2O$ (Aldrich, USA); $Ni(ClO_4)_2\cdot 6H_2O$ (Alfa Asear, UK); 37% formaldehyde solution and triethylamine (S. D. Fine Chemicals, Mumbai, India). The ligand 6,6′-{(2-(dimethylamino)ethylazanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol) was prepared by adapting a literature procedure.[20]

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 500.0 MHz in $CDCl_3$ solutions. 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 these 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.

Magnetic measurements were performed using a Quantum Design SQUID-VSM magnetometer. Magnetization measurements at different fields at a given temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder, and diamagnetism was estimated from Pascal constants. The samples were blocked in eicosane to prevent orientation under a magnetic field.

X-ray Crystallography. Single-crystal X-ray structural studies of **1**−**5** were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The crystals did not degrade/decompose during data collection. Data collection, structure solution, and refinement were performed using SMART, SAINT, and SHELXTL programs, respectively.[21a−f] All the calculations for the data reduction were done using the Bruker SADABS program. All the non-hydrogen atoms were refined anisotropically using full-matrix least-squares procedures. All the hydrogen atoms were included in idealized positions, and a riding model was used. Large solvent-accessible voids remain in all the structures. They are presumably filled with several disordered molecules of dichloromethane, acetonitrile, methanol, and water, which could not be modeled by the present analysis. Therefore, the "PLATON/"SQUEEZE"[21g,h] program was used to remove those disordered solvent molecules. The PLATON-SQUEEZE routine reports that the total solvent-accessible void volumes (per unit cell) are 3690 (for **1**); 3983 (for **2**); 3766 (for **3**); 3819 (for **4**); and 4135 (for **5**) Å^3. These volumes are nearly one-quarter of the unit cell volume for each molecule, which is ∼12 500 Å^3. The lattice solvent molecules (complex **1**, $8CH_3CN$, $3CH_2Cl_2$, and H_2O; complex **2**, $5CH_2Cl_2$ and $5H_2O$; complex **3**, $15CH_3CN$, $18CH_2Cl_2$, $3CH_3OH$, and $2H_2O$; complex **4**, $15CH_3CN$, $20CH_2Cl_2$, $6CH_3OH$, and $5H_2O$; and complex **5**, $3CH_2Cl_2$ and $2CH_3OH$) could not be modeled satisfactorily due to the presence of heavy disorder and were removed by using the SQUEEZE routine of PLATON. The total electron count removed by this routine corresponded to 623 (for complex **1**); 518 (for complex **2**); 2023 (for complex **3**); 2154 (for complex **4**); and 643 (for complex **5**) per unit cell. This corresponds to 311, 259, 1011, 1177, and 160 electrons per molecule ($Z = 2$ for complexes **1**−**4** and $Z = 4$ for complex **5**). All the mean plane analyses as well as molecular drawings were obtained from DIAMOND (version 3.1).

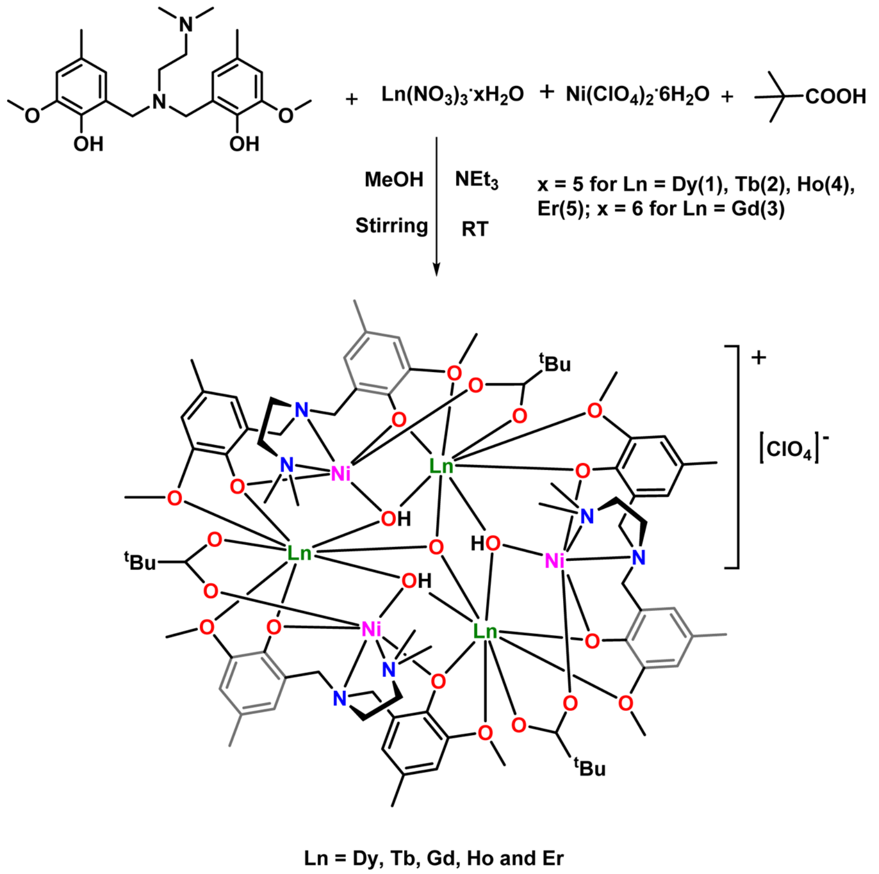
Syntheses. *Preparation of 6,6′-{(2-(Dimethylamino)ethylazanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol) (LH_2).* The synthesis of LH_2 was carried out by an adaptation of the literature procedure.[20] To an ethanolic (40 mL) stirred solution of 2-methoxy-4-methylphenol (2.180 g, 15.78 mmol) were added *N*,*N*-dimethylethylenediamine (0.695 g, 7.884 mmol), a 37% formaldehyde solution (2.376 g, 79.12 mmol), and triethylamine (1.597 g, 15.78 mmol), and the solution was heated under reflux for 3 days (Scheme 1). After this, the solvent was stripped off the solution in vacuo, and the resulting oil was kept in a refrigerator overnight and triturated with petroleum ether and diethyl ether to afford a colorless solid, which was filtered and dried in air affording LH_2. Yield: 1.56 g (51%). Mp: 116 °C. IR (KBr), cm^{-1}: 3424(br), 2986(w), 2939(w), 2833(s), 2781(w), 1589(s) 1500(s), 1466(s), 1381(s), 1358(s), 1325(w), 1283(s), 1262(s), 1225(s), 1157(s), 1128(s), 1106(s), 1082(s), 1045(s), 988(w), 977(w), 935(s), 895(w), 844(s), 814(s), 782(s), 748(w), 596(w), 554(w), 430(w). The ^1H and ^{13}C NMR data are given in the Supporting Information (Figures S1, S2). ESI-MS (m/z): 389.2441 $(M + H)^+$. Anal. Calcd for $C_{22}H_{32}N_2O_4$: C, 68.01.16; H, 8.30; N, 7.21. Found: C, 67.72; H, 8.03; N, 6.96.

Preparation of the Hexanuclear Complexes 1−5. The general synthetic protocol that was used for the preparation of the metal complexes (**1**−**5**) is as follows: A methanolic solution (5 mL) of $Ln(NO_3)_3\cdot nH_2O$ (3 equiv) was added dropwise, under constant stirring, to a 20 mL methanolic solution containing a mixture of LH_2 (2 equiv) and triethylamine (8 equiv) with constant stirring. To this reaction mixture was added solid $Ni(ClO_4)_2\cdot 6H_2O$ (3 equiv), and the reaction mixture was stirred for a further 1.5 h. A deep green-colored solution was obtained. At this stage pivalic acid (4 equiv) was added, and reaction mixture stirred again for 12 h, and the solvent was stripped off in vacuo, resulting in a green solid, which was washed with diethyl ether (3 × 5 mL), redissolved in acetonitrile/dichloromethane (1:1), and filtered. The filtrate was kept for crystallization under slow evaporation at room temperature. After 1 week, green, block-shaped crystals suitable for X-ray analysis were isolated. The quantity of the reactants used in each reaction and the characterization data of the compounds are given below.

*$[Ni_3Dy_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot 8CH_3CN\cdot 3CH_2Cl_2\cdot 5.5H_2O$ (**1**).* $Ni(ClO_4)_2\cdot 6H_2O$ (0.062 g, 0.169 mmol), $Dy(NO_3)_3\cdot 5H_2O$ (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) were used. Yield: 0.096 g, 57% (based on Dy). Mp: >240 °C. IR (KBr, ν/cm^{-1}): 3584(br), 2955(s), 2867(w), 2678(m), 2491(w), 1588(s), 1565(s), 1498(s), 1465(s), 1418(s), 1383(s), 1359(m), 1302(m), 1267(w), 1252(s), 1229(s), 1154(s), 1105(s), 1080(s), 1032(s), 978(w), 933(m), 905(w), 832(s), 783(w), 629(s), 598(s), 503(w), 469(s). Anal. Calcd for $C_{100}H_{161}Cl_7Dy_3N_{14}Ni_3O_{31.5}$ (2975.17): C, 40.37; H, 5.45; N, 6.59. Found: C, 40.06; H, 5.23; N, 6.39.

*$[Ni_3Tb_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot 5CH_2Cl_2\cdot 6.5H_2O$ (**2**).* $Ni(ClO_4)_2\cdot 6H_2O$ (0.062 g, 0.169 mmol), $Tb(NO_3)_3\cdot 5H_2O$ (0.074 mg, 0.170 mmol), LH_2 (0.044 g, 0.113 mmol), Et_3N (0.046 g, 0.454

Scheme 2. Synthesis of Complexes 1−5



mmol), and pivalic acid (0.023 g, 0.223 mmol) were used. Yield: 0.090 g, 56% (based on Tb). Mp: >240 °C. IR (KBr, ν/cm^{-1}): 3587(br), 2956(s), 2923(s), 2867(m), 2840(w), 1706(w), 1586(s), 1564(s), 1497(s) 1484(s), 1464(s), 1419(s), 1373 (s), 1359(s), 1340(s), 1302(m), 1268(s), 1251(m), 1229(s), 1154(s), 1103(s), 1092(s), 1080(s), 1032(s), 978(s), 934(s), 905(m), 831(s), 783(w), 629(s), 598(s), 571(w), 502(m), 468(s). Anal. Calcd for $C_{86}H_{143}Cl_{11}Tb_3N_6Ni_3O_{32.5}$ (2823.91): C, 36.58; H, 5.10; N, 2.98. Found: C, 36.26; H, 4.86; N, 2.78.

$[Ni_3Gd_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot 15CH_3CN\cdot 18CH_2Cl_2\cdot 3MeOH\cdot 7.5H_2O$ *(**3**).* $Ni(ClO_4)_2\cdot 6H_2O$ (0.062 g, 0.169 mmol), $Gd(NO_3)_3\cdot 6H_2O$ (0.077 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, 0.225 mmol) were used. Yield: 0.109 g, 41% (based on Gd). Mp: >240 °C. IR (KBr, ν/cm^{-1}): 3507(br), 2956(s), 2922(s), 2868(s), 2841(m), 1706(w), 1559(s), 1497(s), 1483(s), 1466(s), 1416(s), 1374(s), 1359(s), 1280(m), 1264(s), 1227(s), 1192(w), 1155(s), 1101(s), 1081(s), 1029(s), 976(w), 947(m), 933(s), 889(w), 832(s), 787(s), 748(w), 624(s), 601(s), 568(m), 505(w), 467(s), 445(s). Anal. Calcd for $C_{132}H_{228}Cl_{37}Gd_3N_{21}Ni_3O_{36.5}$ (4652.93): C, 34.07; H, 4.94; N, 6.32. Found: C, 33.82; H, 4.68; N, 6.09.

$[Ni_3Ho_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot 15CH_3CN\cdot 20CH_2Cl_2\cdot 6MeOH\cdot 9.5H_2O$ *(**4**).* $Ni(ClO_4)_2\cdot 6H_2O$ (0.062 g, 0.169 mmol), $Ho(NO_3)_3\cdot 5H_2O$ (0.75 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) were used. Yield: 0.112 g, 40% (based on Ho). Mp: >240 °C. IR (KBr, ν/cm^{-1}): 3588(br), 2955(s), 2869(s), 2801(w), 2739(m), 2678(s), 2491(m), 1704(w), 1590(s), 1566(s), 1499(s), 1465(s), 1433(s), 1418(s), 1383(s), 1359(s), 1302(m), 1269(w), 1252(m), 1229(s), 1154(s), 1108(w), 1080(s), 1033(s), 979(m), 934(w), 906(w), 832(s), 783(w), 637(s), 597(s), 470(s). Anal. Calcd for $C_{137}H_{248}Cl_{41}Ho_3N_{21}Ni_3O_{41.5}$ (4977.99): C, 33.05; H, 5.02; N, 5.91. Found: C, 32.76; H, 4.78; N, 5.72.

$[Ni_3Er_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot 3CH_2Cl_2\cdot 2MeOH\cdot 3H_2O$ *(**5**).* $Ni(ClO_4)_2\cdot 6H_2O$ (0.062 g, 0.169 mmol), $Er(NO_3)_3\cdot 5H_2O$ (0.075 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) were used. Yield: 0.086 g, 57% (based on Er). Mp: >240 °C. IR (KBr, ν/cm^{-1}): 3585(br), 3501(br), 2924(s), 2955(s), 2855(s), 1705(w), 1590(s), 1565(s), 1500(s), 1483(s), 1463(s), 1433(s), 1418(s), 1373(s), 1358(s), 1300(w), 1258(w), 1228(s), 1155(s), 1105(s), 1080(s), 1030(s), 978(w), 935(m), 905(w), 832(s), 783(w), 643(w), 628(w), 600(s), 568(m), 507(w), 471(s). Anal. Calcd for $C_{86}H_{140}Cl_7Er_3N_6Ni_3O_{31}$ (2669.33): C, 38.54; H, 5.27; N, 3.14. Found: C, 38.22; H, 5.04; N, 2.89.

■ RESULTS AND DISCUSSION

Synthetic Aspects. The multisite coordination ligand LH_2 was prepared by a one-pot synthesis employing the Mannich condensation of the corresponding phenol, amine, and formaldehyde.[20] The design of this ligand was based on the observation in the literature that structurally similar ligands possessing alkyl substituents (instead of the −OMe in the current instance) afforded mononuclear complexes (Supporting Information, Schemes S1−10). On the other hand, LH_2 possesses six coordinating sites including potential bridging phenolate oxygen. Also, although not strictly a compartmental ligand, LH_2, by virtue of possessing the −OMe groups, has specific sites that can interact with lanthanide ions while leaving other sites for interacting with transition metal ions. The use of pivalic acid as a coligand was to allow consolidation of the heterometallic framework through possible bridging coordination action. In accordance with the above design strategy, LH_2 reacts with $Ni(ClO_4)_2\cdot 6H_2O$, $Ln(NO_3)_3\cdot nH_2O$, NEt_3, and pivalic acid to afford heterometallic hexanuclear monocationic

Table 1. Crystal Data and Structure Refinement Parameters of **1**−**5**

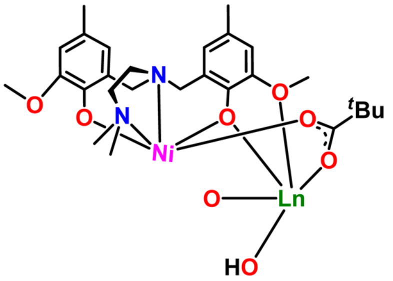
		1	2	3	4	5
formula		$C_{162}H_{240}Cl_2Dy_6N_{12}Ni_6O_{61}$	$C_{162}H_{240}Cl_2N_{12}Ni_6O_{55}Tb_6$	$C_{162}H_{240}Cl_2Gd_6N_{12}Ni_6O_{63}$	$C_{162}H_{240}Cl_2Ho_6N_{12}Ni_6O_{61}$	$C_{81}H_{120}Cl Er_3N_6Ni_3O_{29}$
fw		4729.70	4612.28	4730.20	4744.28	2355.13
temp (K)		100(2)	100(2)	100(2)	100(2)	100(2)
cryst syst		trigonal	trigonal	trigonal	trigonal	trigonal
space group		$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$
unit cell dimens	$a = b$ (Å)	25.048(5)	25.180(5)	25.212(5)	25.066(5)	24.964(5)
	c (Å)	22.985(5)	22.779(5)	22.745(5)	22.972(5)	23.036(5)
	$\alpha = \beta$ (deg)	90	90	90	90	90
	γ (deg)	120	120	120	120	120
volume (Å^3); Z		12489(4); 2	12508(4); 2	12521(4); 2	12500(4); 2	12433(4); 4
density (Mg m^{-3})		1.258	1.225	1.255	1.260	1.258
abs coeff (mm^{-1})		2.297	2.194	2.090	2.400	2.527
$F(000)$		4764	4656	4772	4776	4740
cryst size (mm)		0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18	0.18 × 0.16 × 0.14	0.20 × 0.18 × 0.16	0.22 × 0.20 × 0.18
θ range (deg)		1.63 to 25.50	2.41 to 25.50	4.14 to 25.03	4.09 to 25.02	2.00 to 28.38
limiting indices		$-30 \leq h \leq 29$	$-25 \leq h \leq 30$	$-30 \leq h \leq 23$	$-25 \leq h \leq 29$	$-33 \leq h \leq 33$
		$-30 \leq k \leq 30$	$-30 \leq k \leq 30$	$-30 \leq k \leq 28$	$-29 \leq k \leq 29$	$-33 \leq k \leq 22$
		$-27 \leq l \leq 12$	$-27 \leq l \leq 27$	$-26 \leq l \leq 27$	$-27 \leq l \leq 27$	$-30 \leq l \leq 30$
reflns collected		65 619	88 168	63 177	63 190	109 357
unique reflns [R_{int}]		7773 [0.0795]	7774 [0.0499]	7343 [0.1029]	7347 [0.0807]	10 367 [0.0604]
completeness to θ		100.0% (25.50°)	99.9% (25.50°)	99.5% (25.03°)	99.5% (25.02°)	99.5% (28.38°)
data/restraints/params		7773/13/388	7774/13/379	7343/12/391	7347/7/370	10367/31/418
GOOF on F^2		1.081	1.031	1.033	1.012	1.049
final R indices [$I > 2\sigma(I)$]		$R_1 = 0.0488$, $wR_2 = 0.1385$	$R_1 = 0.0364$, $wR_2 = 0.0913$	$R_1 = 0.0431$, $wR_2 = 0.1154$	$R_1 = 0.0527$, $wR_2 = 0.1430$	$R_1 = 0.0580$, $wR_2 = 0.1421$
R indices (all data)		$R_1 = 0.0588$, $wR_2 = 0.1464$	$R_1 = 0.0461$, $wR_2 = 0.0954$	$R_1 = 0.0511$, $wR_2 = 0.1192$	$R_1 = 0.0623$, $wR_2 = 0.1478$	$R_1 = 0.0715$, $wR_2 = 0.1490$
largest residual peaks (e Å^{-3})		2.933 and −0.822	2.085 and −0.889	2.106 and −0.732	2.720 and −1.309	3.839 and −1.957

complexes $[Ni_3Ln_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(L)_3(\mu\text{-}OOCCMe_3)_3]\cdot(ClO_4)\cdot w CH_3CN\cdot x CH_2Cl_2\cdot y CH_3OH\cdot z H_2O$ [for **1**, $w = 8$, $x = 3$, $y = 0$, $z = 5.5$; for **2**, $w = 0$, $x = 5$, $y = 0$, $z = 6.5$; for **3**, $w = 15$, $x = 18$, $y = 3$, $z = 7.5$; for **4**, $w = 15$, $x = 20$, $y = 6$, $z = 9.5$; and for **5**, $w = 0$, $x = 3$, $y = 2$, $z = 3$] (Scheme 2; see Experimental Section for details of syntheses). These represent the first examples of the Ni_3/Ln_3 family.

Molecular Structures of Complexes 1−5. The molecular structures of complexes **1**−**5** were determined by single-crystal X-ray crystallography. All of these crystallize in the trigonal system with the $P\bar{3}c1$ space group. The crystallographic parameters of these compounds are given in Table 1. In view of the structural similarities of these compounds the molecular structure of **1** is described as a representative example. The structural details of all other compounds are given in the Supporting Information (Figures S3−S6).

The asymmetric unit of **1** contains one-third of the total molecule, namely, $[NiDy(L)(\mu\text{-}Piv)(\mu_3\text{-}O)(\mu_3\text{-}OH)]$ (Chart 1 and Figure 1). The molecular structure of **1** is given in Figure 2 and Scheme 2. The molecular structure of **1** reveals that it is a monocationic heterometallic hexanuclear complex containing one counter perchlorate anion. The hexanuclear complex is assembled by the cumulative coordination action of $[L]^{2-}$, $[OH]^-$, $[O]^{2-}$, and the pivalate ligand, the coordination modes of all of which are summarized in Chart 2. Each $[L]^{2-}$ holds a trinuclear Dy−Ni−Dy motif together. Thus, the methoxy group binds to Dy (Dy1−O2, 2.614(4) Å; Dy1−O3, 2.646(3) Å), while the phenolate bridges a Ni(II) and the Dy(III) [Ni1−O1,

Chart 1. Asymmetric Unit of Complexes **1**−**5**



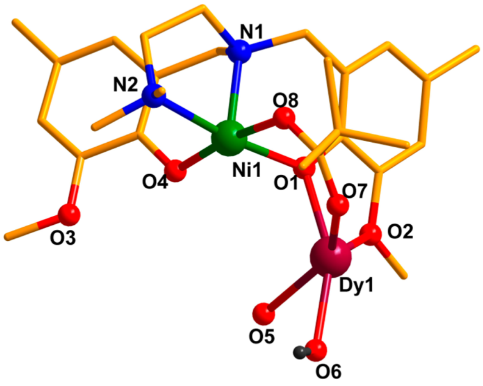


Figure 1. Asymmetric unit of **1** (hydrogen atoms and solvent molecules are omitted for clarity).

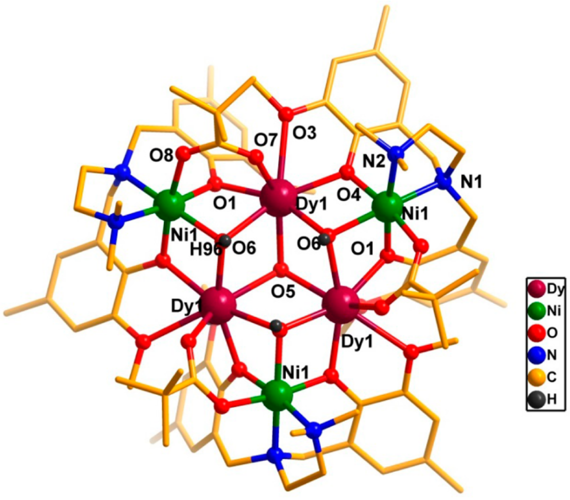
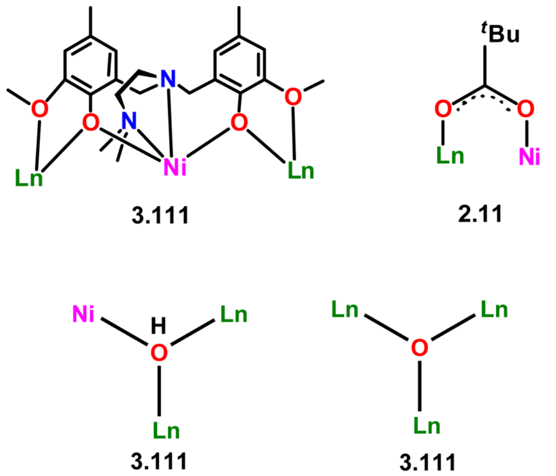


Figure 2. Molecular structure of **1**. All the hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): Dy(1)−O(1), 2.226(3); Dy(1)−O(6), 2.284(4); Dy(1)−O(4), 2.295(3); Dy(1)−O(7), 2.296(4); Dy(1)−O(5), 2.415(3); Dy(1)−O(6)*, 2.426(3); Dy(1)−O(2), 2.614(4); Dy(1)−O(3), 2.646(3); Ni(1)−O(1), 2.019(3); Ni(1)−O(4)*, 2.057(3); Ni(1)−O(8), 2.086(4); Ni(1)−O(6)*, 2.111(4); Ni(1)−N(1), 2.118(4); Ni(1)−N(2), 2.160(4); O(1)−Dy(1)−O(6), 156.69(13); O(1)−Dy(1)−O(4), 130.48(12); O(6)−Dy(1)−O(4), 71.70(12); O(1)−Dy(1)−O(7), 87.43(13); O(6)−Dy(1)−O(7), 93.47(13); O(4)−Dy(1)−O(7), 105.00(13); O(1)−Dy(1)−O(5), 91.88(11); O(6)−Dy(1)−O(5), 74.23(14); O(4)−Dy(1)−O(5), 101.77(10); O(7)−Dy(1)−O(5), 145.18(16); O(1)−Dy(1)−O(6)*, 70.24(12); O(6)−Dy(1)−O(6)*, 87.43(17); O(1)−Dy(1)−O(2), 62.30(11); O(6)−Dy(1)−O(2), 128.46(12); O(4)−Dy(1)−O(2), 75.84(12); O(7)−Dy(1)−O(2), 133.55(13); O(5)−Dy(1)−O(2), 74.58(16); O(1)−Dy(1)−O(3), 77.93(12); O(6)−Dy(1)−O(3), 124.27(11); O(4)−Dy(1)−O(3), 62.67(11); O(7)−Dy(1)−O(3), 70.59(12); O(5)−Dy(1)−O(3), 143.04(16); O(1)−Ni(1)−O(4)*, 89.13(14); O(1)−Ni(1)−O(8), 89.62(14); O(4)*-Ni(1)−O(8), 171.69(14); O(1)−Ni(1)−O(6)*, 80.94(14); N(1)−Ni(1)−N(2), 85.71(17).

Chart 2. Binding Modes of the Ligands Observed in the Present Study



2.019(3) Å; Dy1−O1, 2.226(3) Å; Ni1−O4, 2.057(3) Å; Dy1−O4, 2.295(3) Å]. The two nitrogen centers of [L]$^{2-}$ bind exclusively to Ni(II) [Ni1−N1, 2.118(4) Å; Ni1−N2, 2.160(4) Å]. In addition, three pivalate ligands bridge alternate Ni/Dy pairs through a η^1,η^1 coordination mode [Ni1−O8, 2.086(4) Å; Dy1−O7, 2.296(4) Å]. Three [OH]$^-$ ligands function in a μ-3 manner by bridging one nickel and two lanthanide centers [Ni1−O6, 2.111(4) Å; Dy1−O6, 2.284(4) Å; Dy1−O6*, 2.426(3) Å]. Finally a lone [O]$^{2-}$ bridges the three lanthanide centers in a μ-3 fashion [Dy1−O5, 2.415(3) Å]. The core structure of **1** consists of four incomplete cubic subunits that can be termed as O-capped clusters, analogous to that found in organostannoxane chemistry[22] (three Dy$_2$NiO$_4$ units and one Dy$_3$O$_4$ unit), each of which has a missing vertex (Figure 3).

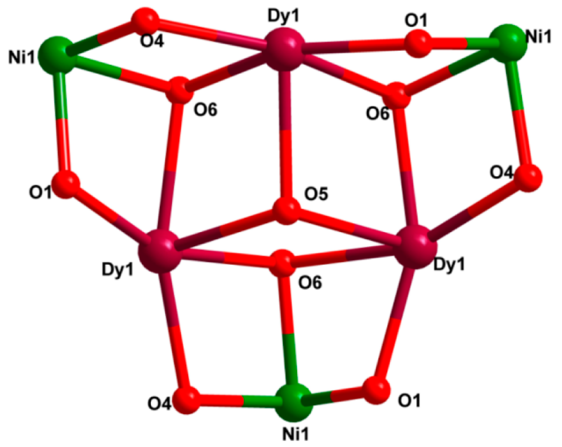


Figure 3. Core structure of compound **1**.

Such structural motifs are known in the literature.[23] It may also be mentioned that the presence of Ni$_4$O$_4$ and Dy$_4$O$_4$ cubic motifs is known.[24,25] All the Ni(II) centers in **1** are equivalent and are hexacoordinate (2N, 4O) in a distorted octahedral geometry (Figure 4a). The Dy(III) centers are also equivalent and are eight-coordinate in a distorted trigonal dodecahedral geometry (Figure 4b). A mean plane analysis of the core of **1** reveals that while the three Ni(II) centers are coplanar and are present in one plane, the three Ln(III) centers are also coplanar but present in a different plane that is parallel to the former (Figure 5). Several metal-containing rings are generated in the structure of **1**, the sizes of which vary from 4 to 12 (Figure S7).

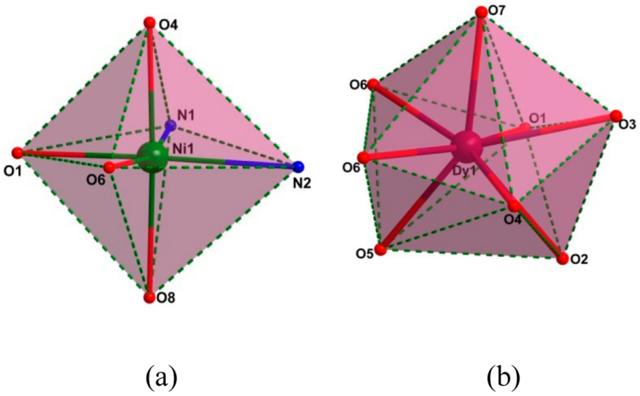


Figure 4. Coordination geometry around the metal centers in **1**: (a) Ni center, distorted octahedron; (b) Dy center, distorted trigonal-dodecahedron geometry.

Magnetic Studies. Magnetic measurements as a function of the temperature were performed on polycrystalline samples in the temperature range 1.8−300 K, under a dc magnetic field of 0.05 T. The χT values at room temperature (44.8 emu·K·

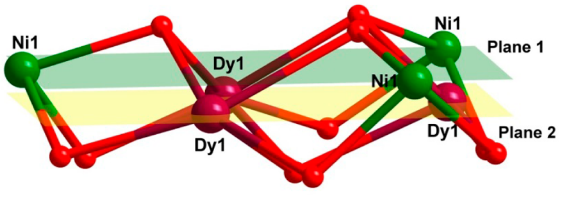


Figure 5. Mean planes of **1**.

mol^{-1} for **1**, 39.7 emu·K·mol^{-1} for **2**, 27.3 emu·K·mol^{-1} for **3**, 46.2 emu·K·mol^{-1} for **4**, 38.5 emu·K·mol^{-1} for **5**) are in good agreement with the expected values for compounds made of three Ni(II) ions ($S = 1$, $g = 2.1$, $C = 1.10$ emu·K·mol^{-1}) and three Dy(III) ($S = 5/2$, $L = 5$, ${}^6H_{15/2}$, $g = 4/3$, $C = 14.17$ emu·K·mol^{-1}) for **1**, three Tb(III) ($S = 3$, $L = 3$, ${}^7F_6$, $g = 3/2$, $C = 11.81$ emu·K·mol^{-1}) for **2**, three Gd(III) ($S = 7/2$, $L = 0$, ${}^8S_{7/2}$, $g = 2$, $C = 7.88$ emu·K·mol^{-1}) for **3**, three Ho(III) ($S = 2$, $L = 6$, ${}^5I_8$, $g = 5/4$, $C = 14.48$ emu·K·mol^{-1}) for **4**, and three Er(III) ($S = 3/2$, $L = 6$, ${}^4I_{15/2}$, $g = 6/5$, $C = 11.48$ emu·K·mol^{-1}) for **5** (Figure 6).[5]

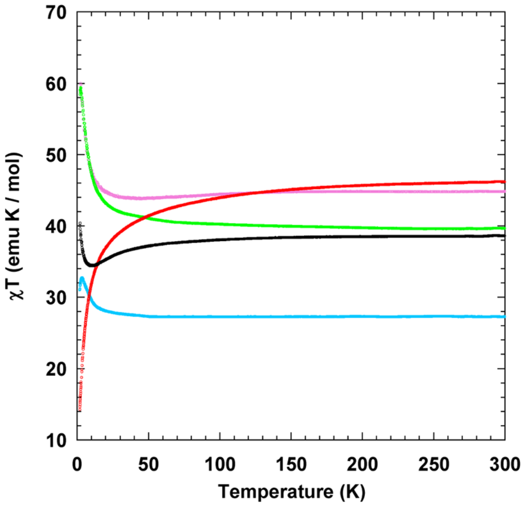


Figure 6. $\chi T = f(T)$ under a static magnetic field of 0.05 T for compounds **1** (purple), **2** (green), **3** (blue), **4** (red), and **5** (black).

Upon decreasing the temperature, the behavior of all compounds are relatively different. For **2** and **3** χT increases gradually up to a maximum at around 3 K. For **1** and **5**, χT decreases to a minimum at around 45 K for **1** and 10 K for **5** before increasing regularly up to 1.8 K. Finally the χT product for the Ho^{III} analogue **4** shows a constant and rapid decrease upon cooling.

For the Gd^{III} analogue **3**, for which there is no spin−orbit coupling, the $\chi T = f(T)$ curve can be fitted considering the following spin-Hamiltonian:

$$\hat{H} = -J_1[\hat{S}_{Ni1}\cdot(\hat{S}_{Gd1} + \hat{S}_{Gd3}) + \hat{S}_{Ni2}\cdot(\hat{S}_{Gd1} + \hat{S}_{Gd2}) + \hat{S}_{Ni3}\cdot(\hat{S}_{Gd2} + \hat{S}_{Gd3})] - J_2(\hat{S}_{Gd1}\cdot\hat{S}_{Gd2} + \hat{S}_{Gd1}\cdot\hat{S}_{Gd3} + \hat{S}_{Gd2}\cdot\hat{S}_{Gd3})$$

(Figure 7) using the Magpack program.[26]

We neglected the magnetic anisotropy of Ni(II) ions, but we had to consider antiferromagnetic intermolecular interaction (within the mean-field approach). The fit leads to $g = 2.01(1)$, $J_1 = 0.96(1)$ cm^{-1}, $J_2 = -0.18$ (1) cm^{-1}, and $zJ = -0.043(1)$ cm^{-1} with a very good agreement factor $R = 1.3 \times 10^{-5}$ (Figure 7). As expected due to the contraction of the 4f orbitals, the magnetic interactions are very weak. The larger Ni−Gd interaction leads to a spin ground state $S = 27/2$.

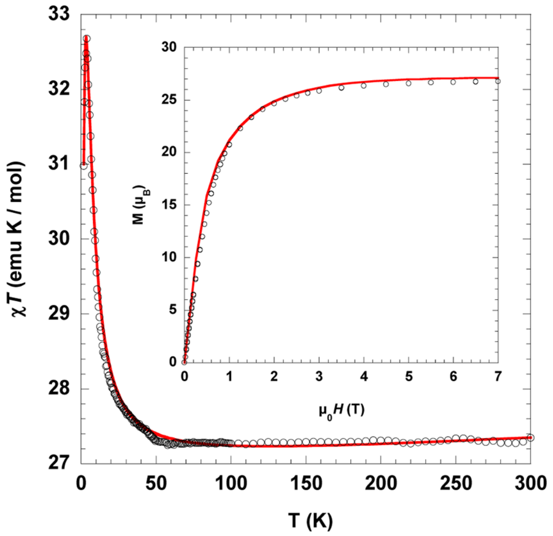


Figure 7. Fit of $\chi T = f(T)$ for compound **3** (open circles: experimental, full line: fit (see text)). Inset: $M = f(H)$ curve for compound **3** (open circles: experimental, full line: calculated curve using the values obtained from the fit of the $\chi T = f(T)$ curve).

The behavior of the other compounds, **1**, **2**, and **5**, can be interpreted as a competition between the thermal depopulation of low-lying crystal-field states of the Ln(III) ions[5] and the Ni(II)−Ln(III) intramolecular ferromagnetic interaction. For **4**, the effect of the thermal depopulation of the excited states of Ho(III) ions most likely dominates the effect of the intramolecular interaction. Therefore, in this case, it is not possible to conclude unambiguously on the nature of the intermolecular interaction, even though the nature of the 3d−4f^n magnetic interaction remains generally the same, with about the same amplitude for Ln(III) ions with $n \geq 7$.[27]

Magnetization versus field measurements at 1.8 K for **1**−**5** are presented in Figure 8. For all compounds, except the

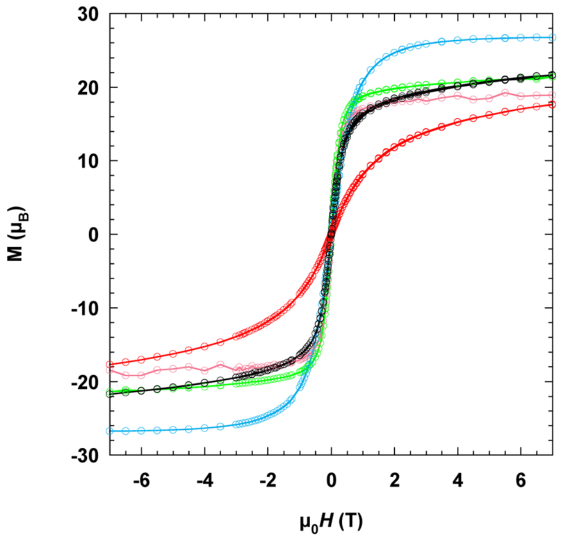


Figure 8. $M = f(H)$ at 1.8 K for compounds **1** (pink), **2** (green), **3** (blue), **4** (red), and **5** (black) (full lines are just a guide for the eye).

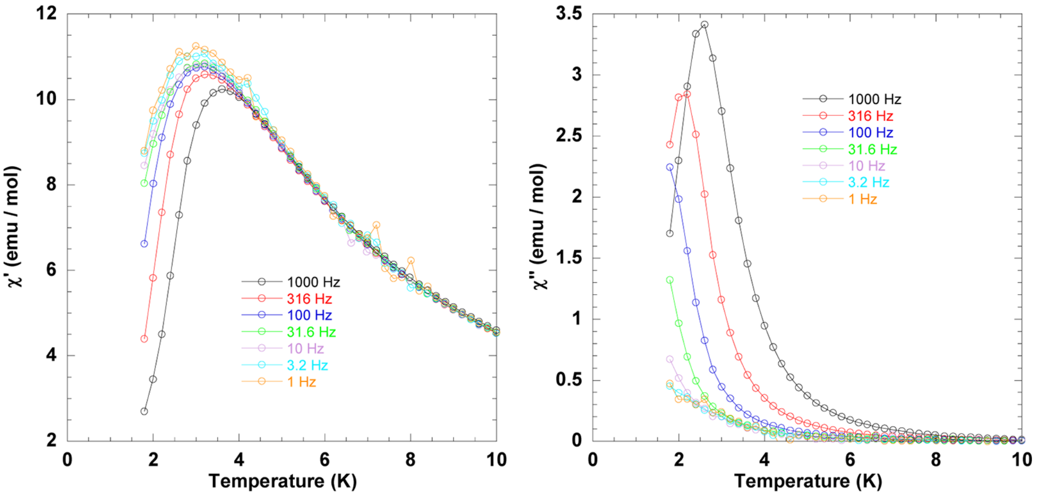


Figure 9. In-phase (left) and out-of-phase (right) susceptibility measurements at various frequencies for compound **1** under an applied dc field of 3000 Oe and with an oscillating field of 2 Oe.

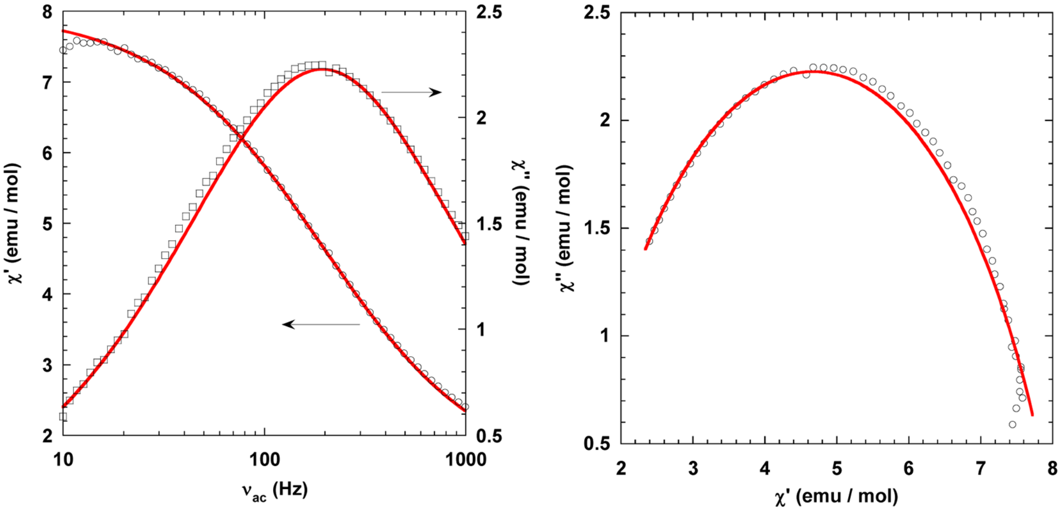


Figure 10. Left: Plots of the in-phase susceptibility (open circles) and out-of-phase susceptibility (open circles) for **1** at 1.8 K (applied dc field of 3000 Oe, oscillating field of 2 Oe). Right: Cole–Cole plot. The solid lines correspond to the fit of the data to a generalized Debye model.

Gd(III) analogue **3**, the magnetization shows a continuous linear increase at high fields, due to the magnetic field-induced population of low-lying excited states. The increase of the magnetization for **4** is clearly slower than for the other compounds, which also indicates the predominance of the crystal-field effect upon intramolecular magnetic interaction. The high-field (7 T) values of the magnetization are 19.0, 21.3, 26.8, 17.6, and 21.7 μ_B for **1**–**5**, respectively, in agreement with the expected ones (between 19.5 and 24 μ_B for **1**, **2**, **4**, and **5** and 27 μ_B for **3**). Indeed, due to crystal-field effects, the values of saturation magnetization for Dy(III), Tb(III), Ho(III), and Er(III) range between 4.5 and 6 μ_B.[28] For **3**, the expected value is higher, around 27 μ_B, because the $^8S_{7/2}$ ground state of Gd(III) is isotropic.

Alternating current susceptibility measurements were performed in a 0 dc static field in the temperature range 1.8–20 K with a 2 Oe field oscillating at frequencies ranging from 1000 to 1 Hz. For compounds **2**–**5**, the in-phase signals are all superimposable, whatever the frequency, and no out-of-phase signal appears down to 1.8 K. On the contrary, for the Dy^{III} derivative **1**, both in-phase and out-of-phase curves show a clear frequency dependence, which suggests a slow relaxation of the magnetization (Figure S8). In order to overcome this difficulty, ac susceptibility measurements were performed under a small optimized dc field (3000 Oe) (Figure S9). Only **1** showed maxima in the temperature dependence of χ' and χ'' under this dc field (Figure 9). Given the very low temperature at which they occur, it is possible to extract only two maxima from this experiment. Therefore, the nature of the relaxation mechanism cannot be ascertained unambiguously as a thermally activated process. From a "fit" to an Arrhenius law, we can estimate a very small energy barrier of about 10 K, with a pre-exponential factor of about 10^{-6} s, within the range of values usually found for other SMMs.

The low-temperature frequency-dependent ac susceptibility data for compound **1** were further analyzed using a generalized Debye model to fit the Cole–Cole plot (see Supporting Information for the fit information) (Figure 10).[29] The best fit of the Cole–Cole plot at 1.8 K leads to the following parameters: α = 0.262(4), χ_0 = 8.07(2) emu·mol^{-1}, χ_∞ = 1.27(3) emu·mol^{-1}, and τ = 0.000 818(8) s. The values of α and τ are consistent with ones usually encountered for other SMMs. The relatively large value for α indicates a broad distribution of relaxation times, suggesting that more than one relaxation process might operate at this temperature.

CONCLUSION

In summary, we have utilized a noncompartmental multiple pocket containing hetero donor chelating mannich base ligand 6,6′-{(2-(dimethylamino)ethylazanediyl)bis(methylene)}bis(2-methoxy-4-methylphenol) to assemble heterometallic mono-cationic hexanuclear Ni(II)−Ln(III) coordination complexes. All these compounds possess homo- and heterometallic O-capped structural subunits (three Ln_2NiO_4 units and one Ln_3O_4 unit), each of which has a missing vertex). All reported complexes represent the first family of Ni_3Ln_3 coordination clusters with this ligand. All the lanthanides centers are eight-coordinate in a distorted trigonal dodecahedral geometry, while nickel centers are hexacoordinated in a distorted octahedral geometry. Magnetic studies reveal an out-of-phase signal for the Dy(III) analogue in its dynamic magnetization studies. Among all these complexes, **1** shows a very small energy barrier of about 10 K, with a pre-exponential factor of about 10^{-6} s.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Schemes representing the reported mononuclear complexes. Figures and tabulated bond angles/lengths for the crystal structures of compounds **2**−**5**. Alternating current susceptibility measurement data under 0 and applied dc field for **1**. Cole−Cole plots fit equations. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vc@iitk.ac.in; vc@niser.ac.in.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Department of Science and Technology, India, and the Council of Scientific and Industrial Research, India, for financial support. V.C. is thankful to the Department of Science and Technology, for a JC Bose fellowship. J.G. thanks the Council of Scientific and Industrial Research, India, for a Senior Research Fellowship.

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