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Syntheses, Structures, and Magnetic Analyses of a Family of Heterometallic Hexanuclear [Ni_4M_2] (M = Gd, Dy, Y) Compounds: Observation of Slow Magnetic Relaxation in the Dy^{III} Derivative

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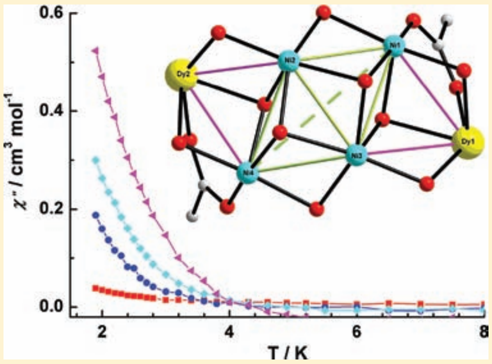
Supporting Information

ABSTRACT: We described the syntheses, crystal structures, and magnetic behavior of a novel series of heterometallic [Ni_4M_2] [M = Gd (**1**), Dy (**2**) and Y (**3**)] hexanuclear compounds afforded by the reaction of rare-earth(III) nitrate, nickel(II) acetate, and Schiff-base ligand 2-(2-hydroxy-3-methoxybenzylideneamino)phenol (H_2L) in a mixture of ethanol and dichloromethane in the presence of triethylamine. Single-crystal X-ray diffraction measurements reveal that all three compounds have a metal core made up of two Ni_2MO_4 defective cubanes. The magnetic properties of all compounds have been studied. Solid-state direct-current magnetic susceptibility analyses demonstrate competing antiferromagnetic and ferromagnetic interactions within both compounds **1** and **3**. Solid-state alternating-current magnetic susceptibility investigations show a frequency-dependent out-of-phase signal for compound **2** below 4 K, suggestive of slow magnetic relaxation.



INTRODUCTION

The design, synthesis, and magnetic investigation of single-molecule-magnets (SMMs)[1] have attracted widespread attention in the past 2 decades because each individual molecule of SMMs can act as a single-domain nanomagnet at a certain blocking temperature in the absence of an external magnetic field, retaining its magnetization once magnetized.[1] SMMs have been considered as potential candidates for the development of information storage and quantum computing devices.[2] Initially, efforts devoted to the quest for SMMs have mainly concentrated on transition-metal[3] clusters, with the majority of them Mn clusters[4] and, in particular, some Mn^{III} centers,[5] which have uniaxial anisotropy in its high-spin state. Moreover, SMMs incorporating $Fe^{II/III}$,[6] Co^{II},[7] and Ni^{II}[3a] ions have also been reported. Frustratingly, the blocking temperature of these described SMMs remained low. As a result, intense current interest to construct SMMs with higher blocking temperatures tends to be focused on mixed-metal systems containing both lanthanide and transition-metal ions.[8] Thus, a number of 3d–4f heterometallic clusters showing SMM properties have been documented, varying in nuclearity numbers from 2[9] to 32[10] and displaying a variety of structure topologies ranging from linear,[11] diamond,[12] star,[13] cyclic,[14] ring,[15] to dicubanes,[16] tricubanes,[17] bell,[18] double-propeller[19] as well as other aesthetically unusual and irregular structural motifs.[20] The majority of these SMMs have involved $Ln^{III}–Mn^{II/III/IV}$,[12,16a,18] $Ln^{III}–Fe^{II/III}$,[9a,11a] $Ln^{IIII}–Co^{II}$,[11c] $Ln^{III}–Ni^{II}$[9d,11a,13a,16d,21] and $Ln^{III}–Cu^{II}$.[11b,14,22] In particular, most of such systems presented so far contain heavy lanthanides such as Tb^{III} or Dy^{III}, which possess significant inherent magnetic anisotropy arising from the large unquenched orbital angular momentum as well as several unpaired spins.[23] It is noteworthy that syntheses of $Ln^{III}–Ni^{II}$-based SMMs remain relatively scarce.[9d,11a,13a,16d,21] Moreover, the $Ln^{III}–Ni^{II}$ combination is an appealing candidate for SMMs because Ni^{II} ions generally exhibit large anisotropy due to its second-order orbital angular momentum.[16d,24]

It is well recognized that the selection of the ligand is crucial to the preparation of 3d–4f heterometallic compounds. A typical approach is based on a one-pot procedure, involving a mixture of 3d and 4f metal salts, and a carefully chosen ligand features distinct functionalities for preferential binding of the 3d and 4f ions. Polydentate chelating Schiff-base ligands are appealing for mixed-metal systems because the chemical characteristics of the polydentate (N and O atoms) can fulfill the coordination affinities to 3d and 4f metal ions for N and O atoms. In fact, there are several examples of 3d–4f compounds derived from this class of ligands.[9c,d,11c,17a,21a] In the present work, we have employed (*E*)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol (H_2L; Scheme 1) in Ni–M (M stands for rare-earth metal ions) cluster chemistry. This

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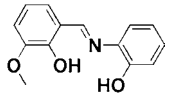
Scheme 1. Structure of the H_2L Ligand



ligand had been used previously to prepare homometallic clusters[25] and had very recently been exploited in 3d−M heterometallic systems.[16d] Herein we report a family of Ni_4M_2 clusters consisting of two Ni_2MO_4 defective cubanes with unusual structural features and magnetic properties, including slow magnetic relaxation for the Ni_4Dy_2 member.

■ EXPERIMENTAL SECTION

Materials and Synthesis. All starting materials were of analytical reagant grade and were used as received without further purification. 2-(2-Hydroxy-3-methoxybenzylideneamino)phenol (H_2L) was prepared by condensation of 2-aminophenol and *o*-vanillin in a 1:1 molar ratio in hot ethanol according to a modified procedure reported previously.[26] All reactions were carried out under aerobic conditions.

Preparation of Compound $[Ni_4Gd_2(\mu_3\text{-}OH)_2(L)_4(OAc)_2(NO_3)_2(H_2O)_2]\cdot 5C_2H_5OH\cdot H_2O$ (1). A methanolic solution of triethylamine (0.65 mL, 0.30 mmol) was added to the Schiff-base H_2L ligand (0.15 mmol, 40 mg) dissolved in 8 mL of ethanol. The reaction mixture was stirred for 40 min. Next, solid gadolinium nitrate hexahydrate (0.15 mmol, 66 mg) was added to the above mixture, and the resulting solution was stirred for 3 h. Solid nickel acetate tetrahydrate (0.15 mmol, 40 mg) was added and further stirred for 2 h. A total of 8 mL of dichloromethane was subsequently added, and the reaction mixture was filtered and then left unperturbed to allow the slow evaporation of the solution. Brown block single crystals, suitable for X-ray diffraction analysis, were obtained after 3 weeks. These crystals were collected by filtration, washed with cold ethanol, and dried in air. Yield: 26 mg (33%, based on the ligand). Elem anal. Calcd for $C_{70}H_{88}N_6O_{32}Ni_4Gd_2$: C, 40.52; H, 4.27; N, 4.05. Found: C, 40.24; H, 3.91; N, 3.95. IR (KBr, cm^{-1}): 3383(m), 3061(m), 2947(m), 1617(s), 1587(s), 1556(s), 1489(s), 1463(s), 1435(s), 1387(s), 1310(s), 1295(m), 1279(w), 1255(m), 1229(s), 1183(s), 1112(w), 1095(w), 1076(w), 1037(w), 968(m), 878(w), 858(w), 824(m), 783(w), 739(s), 661(w), 642(m), 618(w), 579(w), 555(w), 516(m), 444(w).

Preparation of Compound $[Ni_4Dy_2(\mu_3\text{-}OH)_2(L)_4(OAc)_2(NO_3)_2(H_2O)_2]\cdot 4C_2H_5OH\cdot 2H_2O$ (2). This compound was obtained as brown block crystals according to the procedure for **1**, using $Dy(NO_3)_3\cdot 6H_2O$ (0.20 mmol, 96 mg) in place of $Gd(NO_3)_3\cdot 6H_2O$. Yield: 23 mg (28%, based on the ligand). Elem anal. Calcd for $C_{68}H_{84}N_6O_{32}Ni_4Dy_2$: C, 39.70; H, 4.11; N, 4.09. Found: C, 39.51; H, 3.75; N, 3.94. IR (KBr, cm^{-1}): 3412(m), 3062(m), 1616(s), 1587(m), 1556(m), 1484(s), 1463(s), 1385(s), 1307(m), 1230(s), 1184(m), 1112(w), 1095(w), 1076(w), 1036(w), 967(m), 877(w), 857(w), 822(m), 739(m), 663(w), 642(w), 579(w), 517(w), 444(w).

Preparation of Compound $[Ni_4Y_2(\mu_3\text{-}OH)_2(L)_4(OAc)_2(NO_3)_2(H_2O)_2]\cdot 5C_2H_5OH\cdot CH_3OH$ (3). This compound was prepared as olive plate crystals following the procedure for **1**, except that $Y(NO_3)_3\cdot 5H_2O$ (0.15 mmol, 58 mg) was used instead of $Gd(NO_3)_3\cdot 6H_2O$. Yield: 20 mg (27%, based on the ligand). Elem anal. Calcd for $C_{71}H_{90}N_6O_{32}Ni_4Y_2$: C, 43.68; H, 4.65; N, 4.31. Found: C, 43.62; H, 4.30; N, 4.21. IR (KBr, cm^{-1}): 3401(m), 3060(m), 2944(m), 1615(s), 1586(s), 1555(s), 1489(s), 1463(s), 1435(s), 1385(s), 1339(w), 1309(s), 1294(m), 1279(m), 1258(m), 1228(s), 1183(s), 1166(w), 1150(w), 1111(w), 1095(m), 1076(w), 1046(w), 960(m), 877(w), 858(w), 825(m), 781(w), 751(m), 738(s), 662(w), 642(m), 618(w), 591(w), 578(w), 554(w), 515(m), 444(w).

Physical Measurements. Elemental analyses for C, H, and N were performed with a VarioEL element analyzer. The IR measurements were recorded on a Vertex 70 Fourier transform infrared spectrophotometer using the reflectance technique (4000−300 cm^{-1}); the samples were prepared as KBr disks. Magnetic measurements were performed from 2 to 300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for the diamagnetic contribution of the sample holder. For magnetization experiments, the temperature was set from 2.0 to 5.0 K and the field was varied from 0 to 7 T. Alternating-current (ac) susceptibility measurements were taken of powdered **1**−**3** to determine the in-phase and out-of-phase components of the magnetic susceptibility. The data were collected by decreasing the temperature from 30.0 to 2.0 K, with no applied external direct-current (dc) field and a drive frequency of 3.0 Oe, with frequencies between 1 and 1000 Hz.

X-ray Crystal Structure Determinations. Suitable single crystals with dimensions of 0.32 × 0.28 × 0.25, 0.25 × 0.21 × 0.19, and 0.23 × 0.21 × 0.18 mm^3 for **1**−**3** were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at a temperature of 191 K for **1**−**3** on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data processing was accomplished with the *SAINT* processing program. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using *SHELXTL97*.[27] The locations of the heaviest atoms (Ni and rare-earth) were easily determined, and the O, N, and C atoms were subsequently determined from the difference Fourier maps. The non-H atoms were refined anisotropiclly. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Selected bond lengths and angles of **13** are summarized in Table S1 in the Supporting Information. CCDC numbers 842927 (**1**), 842928 (**2**), and 842929 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

■ RESULTS AND DISCUSSION

The reaction of rare-earth nitrate salts and nickel acetate with H_2L in a mixture of ethanol and dichloromethane in a 1:1 molar ratio, in the presence of triethylamine, leads to the formation of hexanuclear heterometallic Ni_4M_2 clusters, namely, $[Ni_4M_2(\mu_3\text{-}OH)_2(L)_4(OAc)_2(NO_3)_2(H_2O)_2]\cdot kC_2H_5OH\cdot mCH_3OH\cdot nH_2O$ [M = Gd^{III} with k = 5 and n = 1 (**1**), Dy^{III} with k = 4 and n = 2 (**2**), and Y^{III} with k = 5 and m = 1 (**3**)]. Compounds **13** have analogous molecular structures of clusters, differing in the number and variety of solvent molecules of crystallization; therefore, a full description of the structure of **2** is described here as representative for the whole series. Compounds **1** and **2** crystallize in the monoclinic space group $C2/c$, and the molecular structure of **2** is shown in Figure 1, while that of **3** is found to crystallize in the triclinic space group $P\bar{1}$ (Table 1). Selected bond lengths and angles of **13** are summarized in Table S1 in the Supporting Information. The complex core can be described as two Ni_2DyO_4 defective cubane subunits held together by two hydroxyl groups, two acetate anions, and the O atoms from two deprotonated 3.2211 and two deprotonated 4.3211 coordination-mode[28] ligands. Peripheral ligations are provided by two nitrate anions and two coordinated water molecules. Each Ni_2DyO_4 subunit comprises two Ni ions and one Dy ion arranged as a defective cubane with one missing vertex, in which the three metallic ions are connected to each other by means of three phenoxo groups and one hydroxyl group. In addition, it is worth noting that the phenoxo groups adopt two types of coordination modes connecting the metallic ions. Two of three phenoxo groups adopt a doubly bridged mode, and each connects one Ni ion and one Dy ion, whereas the remaining one adopts a triply bridged mode binding three Ni ions, among which one Ni ion stems from the adjacent

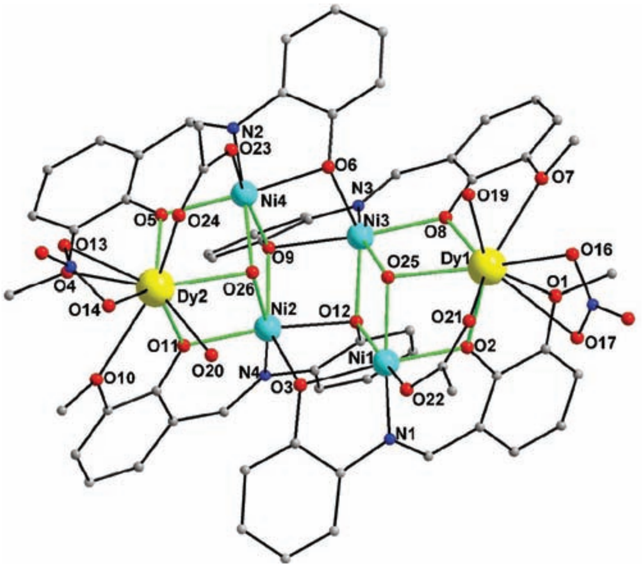


Figure 1. Molecular structure of **2** highlighting the $[Ni_2DyO_4]$ heterometallic defective cubane subunits in bright-green lines. The noncoordinated solvent molecules and H atoms are omitted for clarity.

cubane subunit. Meanwhile, the hydroxyl group just adopts a triply bridged mode linking two Ni ions and one Dy ion.

All four Ni ions are six-coordinated with the NO_5 environment, and the coordination polyhedron can be viewed as distorted octahedral geometry. The equatorial positions of Ni1 and Ni4 are occupied by NO_3 donor atoms from one 3.2211[28] coordination-mode ligand and one μ_3-hydroxyl group, as well as two O atoms from one 4.3211[28] coordination-mode ligand and one acetate anion in the axial positions. Furthermore, the acetate anion binds Ni and Dy ions in a 2.11[28] coordination fashion. The equatorial planes of Ni2 and Ni3 are also composed of NO_3 atoms from one 4.3211[28] ligand and one μ_3-hydroxyl group, and the axial positions are occupied by two O atoms arising from two 3.2211[28] ligands. The Ni−O and Ni−N bond lengths cover ranges 1.998(7)−2.235(6) and 2.000(9)−2.049(9) Å, respectively. All of the NI ion pairs are connected through either phenoxo or hydroxyl groups, forming five edge-sharing Ni_2O_2 planes. Similar tetranuclear nickel topology can be found in other nickel complexes.[29] The values of Ni···Ni separation are in the range 3.0434(18)−5.1628(17) Å. The Ni−O−Ni angles range from 89.1(2) to 105.2(3)°. Dy1 and Dy2 ions have the same nine-coordinated environment, bound by one 3.2211 and one 4.3211 coordination-mode[28] ligand, one coordinated water molecule, one nitrate anion and one acetate anion, as well as one μ_3-hydroxyl group. The Dy−O bond lengths fall in the range of 2.237(7)−2.735(8) Å. Each Dy ion is linked through phenoxo groups and the hydroxyl group toward the central two Ni ions, resulting in a Ni_2DyO_4 defective cubane; these are further bridged by phenoxo groups to adjacent cubane, thus affording a $Ni_4Dy_2O_{10}$ core with two edge-to-edge Ni_2DyO_4 defective cubanes. The Ni···Dy distances range from 3.3104(15) to 5.9855(13) Å.

Magnetic Properties. The temperature dependence of the direct-current (dc) magnetic susceptibilities of compounds **1**−**3** under a constant magnetic field of 1000 Oe was measured in the 2−300 K temperature range. The results are represented in Figure 2 as a $\chi_M T$ versus T curve (χ_M being the molar magnetic susceptibility per $Ni^{II}{}_4M^{III}{}_2$ heterohexanuclear unit). The curves reveal a similar behavior for **1**−**3**. At room temperature, the product of $\chi_M T$ for **3** is 5.25 cm^3 K mol^{-1}, which is in very good agreement with the presence of four independent $S = 1$ Ni^{II} ions ($S = 1$, $C = 1.32$ cm^3 K mol^{-1} with $g = 2.30$) and two diamagnetic Y^{III} ions. This value stays unchanged with

Table 1. Crystal Data and Structure Refinement for Compounds 1−3

	1	2	3
empirical formula	$C_{70}H_{88}N_6O_{32}Ni_4Gd_2$	$C_{68}H_{84}N_6O_{32}Ni_4Dy_2$	$C_{71}H_{90}N_6O_{32}Ni_4Y_2$
F_w (g mol^{-1})	2074.80	2057.25	1952.15
cryst syst	monoclinic	monoclinic	triclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$
cryst color	brown	brown	olive
cryst size (mm^3)	0.32 × 0.28 × 0.25	0.25 × 0.21 × 0.19	0.23 × 0.21 × 0.18
temp (K)	191(2)	191(2)	191(2)
a (Å)	37.0762(19)	36.961(2)	12.8089(9)
b (Å)	23.3078(13)	23.3603(15)	15.9790(11)
c (Å)	22.8546(12)	22.8104(14)	21.7263(15)
α (deg)	90	90	69.7450(10)
β (deg)	124.2130(10)	124.1640(10)	89.5670(10)
γ (deg)	90	90	85.7050(10)
V ($Å^3$)	16332.4(15)	16296.3(18)	4159.4(5)
ρ_{calcd} (Mg m^{-3})	1.688	1.677	1.559
μ (mm^{-1})	2.591	2.802	2.352
$F(000)$	8368	8272	2008
θ for data collection (deg)	1.10−26.06	1.10−25.06	1.36−24.54
collected reflns	45 017	45 137	20 332
indep reflns	16 123	14 413	13 738
R_{int}	0.0378	0.0949	0.0338
R $[I > 2\sigma(I)]$	0.0385	0.0610	0.0623
wR (all data)	0.1192	0.1945	0.1988
GOF on F^2	1.036	0.998	1.040
largest diff peak and hole (e $Å^{-3}$)	−0.881 and 3.231	−1.182 and 3.365	−0.743 and 2.866

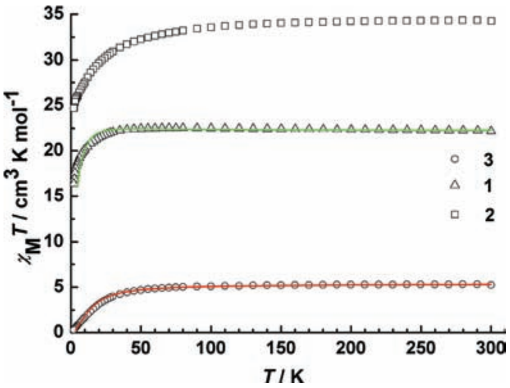


Figure 2. Temperature dependence of the $\chi_M T$ products at 1000 Oe for compounds **1** (triangles), **2** (squares), and **3** (circles). The color lines correspond to the calculated behavior of compounds **1** and **3** (see the text for details).

decreases in temperature until about 50 K, where it decreases to 0.28 cm^3 K mol^{-1} at 2 K. This indicates that the coupling within the cluster is predominantly antiferromagnetic in character. The low-temperature $\chi_M T$ value of 0.28 cm^3 K mol^{-1} is consistent with an $S = 0$ ground state. We were able to successfully simulate the magnetic susceptibility data using the four-*J* models as shown in Scheme 2 (left). Using the *MAGPACK*[30] program and employing the Hamiltonian in eq 1

$$\hat{H} = -2J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_3\cdot\hat{S}_4) - 2J_2(\hat{S}_1\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_4) - 2J_3(\hat{S}_2\cdot\hat{S}_3) - 2J_4(\hat{S}_1\cdot\hat{S}_4) \qquad (1)$$

afforded the parameters $J_1 = 1.4$ cm^{-1}, $J_2 = -4.4$ cm^{-1}, $J_3 = 1.5$ cm^{-1}, $J_4 = -0.45$ cm^{-1}, and $g = 2.32$. Obviously, the value of J_1 is almost equal to that of J_3. Alternatively, adopting three-*J* models can also work well in this simulation procedure. Previous literature reported that Ni−O−Ni angles between any two Ni^{II} ions that are smaller than 98° are expected to result in ferromagnetic coupling. Angles larger than 98° are expected to lead to antiferromagnetic coupling between Ni^{II} ions.[31] In the three cases (J_1, J_2, and J_3), both J_1 and J_3 correspond to the bridging angles smaller than 98°; thus, their values are positive. Moreover, J_2 corresponds to the bridging angles larger than 98°, and its value is negative. Obviously, our results are in very good agreement with the literature report. The antiferromagnetic nature of J_2 may be attributed to countercomplementarity effects[32] between the phenoxo and hydroxyl groups. Magnetic analysis on compound **3** reveals that the exchange coupling is weak and the best fits give weakly coupled exchange couplings that are both ferro- and antiferromagnetic in nature. The magnetization of **3** at 2 K shows a roughly linearly shaped isothermal *M* versus *H* plot, reaching 2.76 μ_B, up to 7 T (Figure 3). ac susceptibility measurements performed in the 2−30 K range in a zero applied dc field and a 3 Oe ac field oscillating at 997 Hz show the complete absence of an out-of-phase component above 2 K (Figure S1 in the Supporting Information).

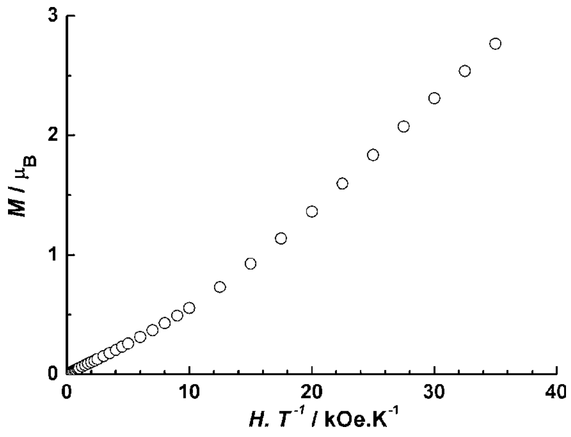
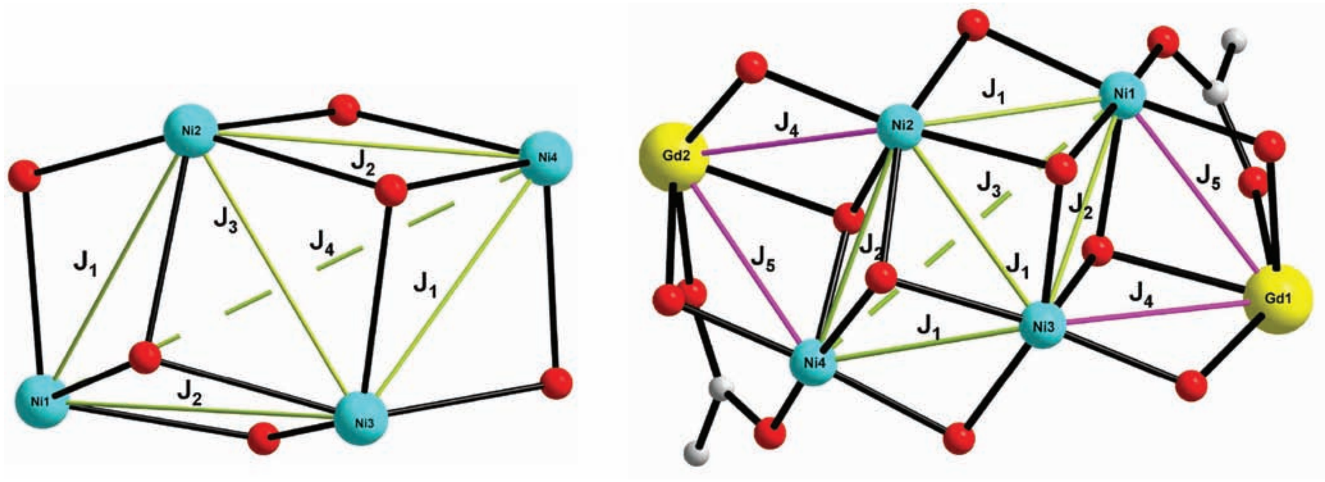


Figure 3. Field dependence of magnetization of compound **3** at 2 K.

The $\chi_M T$ value of 22.17 cm^3 K mol^{-1} at 300 K for **1** is close to the expected value of 21.03 cm^3 K mol^{-1} for four uncoupled Ni^{II} ions ($S = 1$, $C = 1.32$ cm^3 K mol^{-1} with $g = 2.30$) and two uncoupled Gd^{III} ions ($^8S_{7/2}$, $S = {}^7/_2$, and $g = 2$). The $\chi_M T$ product remains essentially constant upon lowering of the temperature until 15 K and below, at which it decreases, reaching a value of 16.40 cm^3 K mol^{-1} at 2 K. The decrease of $\chi_M T$ at low temperature obviously indicates the presence of dominantly intramolecular antiferromagnetic interaction within the molecule. To describe this behavior, fitting the experimental

Scheme 2. Magnetic Exchange Interactions Four-*J* and Five-*J* Models Employed To Simulate the Susceptibilities of Compounds 3 (Left) and 1 (Right)



data was attempted by employing the *MAGPACK*[30] program with the Hamiltonian in eq 2. Five-*J* models were employed in order to avoid overparameterization in the simulation procedure, taking the simulation result of compound **3** and the exchange interactions between Ni2···Gd1 and Ni3···Gd2 as negligible into account.

$$\hat{H} = -2J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_3\cdot\hat{S}_4) - 2J_2(\hat{S}_1\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_4) - 2J_1(\hat{S}_2\cdot\hat{S}_3) - 2J_3(\hat{S}_1\cdot\hat{S}_4) - 2J_4(\hat{S}_2\cdot\hat{S}_{Gd2} + \hat{S}_3\cdot\hat{S}_{Gd1}) - 2J_5(\hat{S}_1\cdot\hat{S}_{Gd1} + \hat{S}_4\cdot\hat{S}_{Gd2}) \qquad (2)$$

The calculation yielded the fit parameters $J_1 = 1.6$ cm^{-1}, $J_2 = -4.0$ cm^{-1}, $J_3 = -0.30$ cm^{-1}, $J_4 = 0.78$ cm^{-1}, $J_5 = -0.31$ cm^{-1}, and $g = 2.12$. The results indicate that both ferro- and antiferromagntic interactions coexist between Ni and Gd ions. In the two cases (J_4 and J_5), J_5 between Ni1···Gd1 and Ni4···Gd2 is triply mediated by one phenoxo group and one hydroxyl group as well as one acetate anion, whereas J_4 between Ni3···Gd1 and Ni2···Gd2 is doubly mediated by one phenoxo group and one hydroxyl group. The antiferromagnetic nature of J_5 may be mainly attributed to the acetate anion.[33]

The magnetization of **1** has also been performed at 2 K (Figure 4). The magnetization at 2 K shows an increase at low field followed by an almost linear increase without clear saturation even at 7 T, in which it reaches 17.85 μ_B. This value is lower than expected (22 μ_B) for two Gd^{III} ($S = {}^7/_2$) ions and four $S = 1$ Ni^{II} ions, which are uncoupled, consistent with the presence of important antiferromagnetic interactions. ac susceptibility measurements performed in the 2−30 K range in a zero applied dc field and a 3 Oe ac field oscillating at 997 Hz show the complete absence of an out-of-phase component above 2 K (Figure S2 in the Supporting Information), which is to be expected because of the isotropic nature of the Gd ion. Extrapolation of the $\chi'_M T$ plot to 0 K gives a value of 20.3 cm^3 mol^{-1} K, suggesting a possible spin ground state of $S = 6$ (Figure S3 in the Supporting Information).[34]

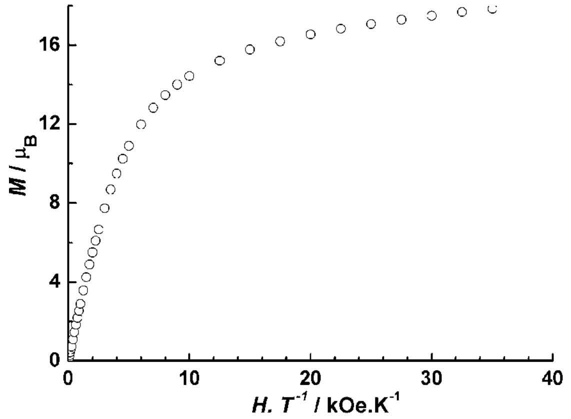


Figure 4. Field dependence of magnetization of compound **1** at 2 K.

At 300 K, the measured $\chi_M T$ value for **2** is 34.28 cm^3 K mol^{-1}, which is in agreement with the calculated value of 33.62 cm^3 K mol^{-1} for four Ni^{II} ions ($S = 1$, $C = 1.32$ cm^3 K mol^{-1} with $g = 2.30$) and two magnetically independent Dy^{III} ions ($^6H_{15/2}$, $S = {}^5/_2$, $L = 5$, $J = {}^{15}/_2$, and $g = {}^4/_3$). Upon cooling, the $\chi_M T$ value decreases slowly up to 100 K, where it reaches a value of 34.02 cm^3 K mol^{-1}, and then decreases rapidly down to 2 K, reaching a minimum value of 24.69 cm^3 K mol^{-1}. The decrease of $\chi_M T$ is most likely due to the combination of the thermal depopulation of the Dy ion excited states (Stark sublevels of the $^6H_{15/2}$ state) and the possible antiferromagnetic interactions between metal centers. The field dependence of magnetization of **2** was collected at low temperatures, as shown in Figure 5. The curves are not all superimposed on a single master curve, implying the presence of significant magnetic anisotropy and/or low-lying excited states. The magnetization eventually reaches the value of 13.65 μ_B for **2** at 2 K and 50 kOe without clear saturation.

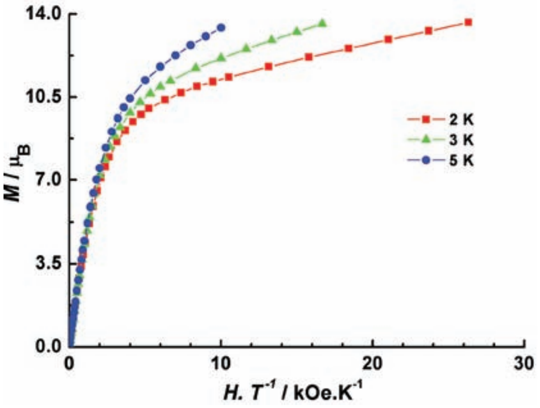


Figure 5. Plot of *M* versus *H*/*T* for **2** in the temperature range below 5 K.

The dynamic magnetic properties of compound **2** were further probed by alternating-current (ac) measurements. ac magnetic susceptibility studies were performed on **2** in the 2−8 K temperature range in a zero applied dc field and a 3 Oe ac field oscillating at frequencies in the 1−1200 Hz range (Figure 6). **2** exhibited a frequency-dependent out-of-phase (χ'') signal below 4 K, but no peaks were found at frequencies lower than 1200 Hz until 1.9 K. Obviously, the slow relaxation of magnetization is evident from ac susceptibility data of **2**. Because no out-of-phase signals were observed for compounds **1** and **3**, we can concluded that the magnetic slow relaxation behavior of compound **2** arises largely from the presence of the anisotropic Dy ion. It is worth mentioning that the dynamic magnetic behavior of **2** is quite different from that of recently reported defective dicubane Ni$_2$Dy$_2$ compounds. Indeed, the

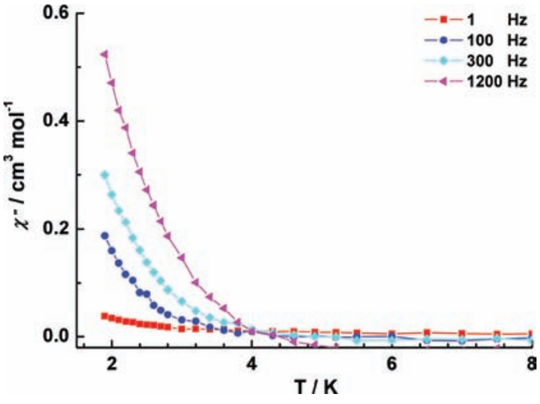


Figure 6. Temperature dependences of out-of-phase (χ'') ac susceptibilities of **2** at different frequencies in a zero dc field and a 3 Oe ac field.

Ni_2Dy_2 compounds are ferromagnetically coupled and are found to be SMMs, while compound **2** shows only a slow magnetic relaxation of magnetization. The strictly planar butterfly core with two Ni^{II} ions in the body positions and each Dy^{III} ion in the wing positions of the Ni_2Dy_2 compounds can be described as the fusion of two Ni_2Dy triangles with shared edges through Ni1 and NiA atoms. However, the dihedral angle between the two separate Ni_2Dy triangles in compound **2** is 68.033°. As observed in compounds **1** and **3**, the presence of additional Ni···Ni edges in **2** compared to the Ni_2Dy_2 compounds might introduce significant antiferromagnetic interactions within the molecules. It is well-known that the magnetic anisotropy of an exchange-coupled system depends not only on the individual anisotropies of the metal ions but also on the relative orientation of the local axes. The distinct anisotropy of the Dy^{III} ions determined by the different coordination environments (eight-coordinated in Ni_2Dy_2 compounds and nine-coordinated in **2**) and ligand fields around the Dy^{III} ion and/or the different relative orientation of the local axes within **2** and Ni_2Dy_2 is mostly responsible for the distinctive relaxation dynamics observed.[16d,35]

■ CONCLUSION

We have reported the syntheses, crystal structures, and magnetic analyses of a new family of heterometallic hexanuclear Ni_4M_2 clusters. The metal core of each cluster is composed of two Ni_2MO_4 defective cubanes. Compound **1** (M = Gd) displays a combination of antiferro- and ferromagnetic coupling pathways, with no SMM features. On the other hand, the incorporation of an anisotropic ion such as Dy in compound **2** led to the observation of slow magnetic relaxation, as demonstrated by a frequency-dependent out-of-phase ac signal. Magnetic analysis on compound **3** indicates Ni···Ni antiferromagnetic exchange interactions competing with ferromagnetic exchange interactions, which is mainly affected by the Ni−O−Ni bridging angles. Efforts to construct other fascinating structures by reacting the H_2L ligand with other rare-earth(III) salts as well as other transition-metal salts are continuing in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected bond lengths and angles for compounds **1**−**3** (Table S1) and additional magnetic data for **1** and **3** (Figures S1−S3). 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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