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# Synthesis, Structures and Magnetism of Heterobinuclear Ni-Ln Complexes: Field-induced Single-molecule Magnetic Behavior in the Dysprosium Analogue

Xing-Yun Lu, Yu-Qing Liu, Xiao-Wei Deng, Zhao-Xia Zhu, Min-Xia Yao,\* and Su Jing\*

*College of Science, Nanjing Tech University, Nanjing, 211816, P. R. China.*

## Abstract

By using the azide anion, hexafluoroacetylacetonato anion (hfac) and compartmental Schiff-base ligand  $H_2valpn$  ( $H_2valpn = 1,3$ -propanediylbis(2-iminomethylene-6-methoxy-phenol)), three isomorphous Ni-Ln heterodinuclear complexes  $[Ni(valpn)Gd(hfac)_2N_3(H_2O)_2] \cdot H_2O$  (**1**),  $[Ni(valpn)Tb(hfac)_2N_3(H_2O)_2] \cdot H_2O$  (**2**) and  $[Ni(valpn)Dy(hfac)_2N_3(H_2O)_2] \cdot H_2O$  (**3**) were synthesized. Structural analyses reveal that the Ni(II) and Ln(III) ions are doubly bridged by two phenoxo oxygen atoms of the valpn ligand. Magnetic susceptibility measurements show ferromagnetic couplings are operative between the Ni(II) and Ln(III) ions in **1–3**. Ac susceptibility measurements under a dc-applied field of 1000 Oe disclose that the Dy derivative exhibits the field-induced single-molecule magnet behavior with effective energy barrier of 16.9 K for reversal of the magnetization.

## Introduction

Since the discovery of  $Mn_{12}$  cluster exhibiting single-molecule magnet (SMM) behavior and the  $Co^{II}$ -radical complex displaying single-chain magnet (SCM) behavior, SMMs/SCMs showing slow magnetic relaxation below the blocking temperature ( $T_B$ ) and can be used as quantum computer and information storage have attracted increasing interest.<sup>1-4</sup> For a SMM, it must possess a large ground-state spin

\* To whom correspondence should be addressed. Email: yaomx@njtech.edu.cn ; sjing@njtech.edu.cn. Fax: +86-25-58139528. Nanjing Tech University.

and strong uniaxial magnetic anisotropy in the cluster, whereas a SCM must possess a large Ising anisotropy, strong intrachain magnetic couplings, and very weak interchain magnetic interactions.<sup>5-8</sup> In the reported SMMs/SCMs constructed from 3d transition-metal ions, the blocking temperatures are generally very low.<sup>9-11</sup> It is well known that lanthanide (Ln) ions (especially Dy<sup>III</sup>, Tb<sup>III</sup>) usually exhibit strong single-ion magnetic anisotropy arising from the large unquenched orbital angular momentum, and show ferromagnetic couplings with 3d transition-metal ions (such as Ni<sup>II</sup>, Cu<sup>II</sup>).<sup>12,13</sup> Moreover, the slow relaxation of the magnetization in 3d-4f SMMs/SCMs mainly origin from the ligand-field effect of the lanthanide ions and the exchange couplings between lanthanide ions and transition-metal ions.<sup>14</sup> Therefore, combining 3d (especially Ni<sup>II</sup> ions with larger ground-state spin and single-ion anisotropy) and 4f ions (such as Dy<sup>III</sup>, Tb<sup>III</sup>) to construct SMMs/SCMs may offer higher effective energy barrier for reversal of the magnetization, or even higher blocking temperatures.<sup>15,16</sup> By introducing the [(Tp\*)Fe(CN)<sub>3</sub>]<sup>-</sup> anion into the [Ni(valpn)Ln](NO<sub>3</sub>)<sub>3</sub> heterodinnuclear unit, we had obtained a series of 3d-3d'-4f heterotirmetallic complexes exhibiting SCMs behaviors.<sup>13d</sup> Among these compounds, the Dy derivate displays the higher effective energy of 58.2 K under a zero applied dc field.

In this study, to continue to explore 3d-4f heterometallic complexes exhibiting SMMs/SCMs behaviors, we intend to synthesize some Ni-Ln complexes. In order to improve the intracluster/intrachain magnetic coupling, the azido anion was chosen as the bridging ligand due to its versatile binding modes and its capacity to mediate different types of magnetic exchange interactions.<sup>17</sup> Here, three heterodinuclear Ni-Ln complexes

$$[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Gd}(\text{hfac})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} \quad (1),$$

$$[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Tb}(\text{hfac})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} \quad (2) \quad \text{and}$$

$$[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Dy}(\text{hfac})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} \quad (3)$$

were successfully synthesized. Their crystal structures and magnetic properties were investigated. Unfortunately, the azide anion, only as the terminal ligand, does not connect the heterodinuclear unit to form larger clusters or one-dimensional chain.

## Experimental Section

### Starting materials

All the reagents were commercially available and used without further purification.

The  $\text{H}_2\text{valpn}$ ,  $\text{Ni}(\text{valpn})(\text{H}_2\text{O})_2$  and  $\text{Ln}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  was synthesized following a published method.<sup>18</sup>

**Caution:** Although no problems were encountered in this work, the azido complexes are potentially explosive. Thus, these starting materials should be handled in small quantities and with great care.

### Syntheses

#### Preparation of $[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Gd}(\text{hfac})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (1)

$\text{Ni}(\text{valpn})(\text{H}_2\text{O})_2$  (0.08mmol, 34.8mg) and  $\text{Gd}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  (0.08mmol, 64.8mg) were mixed in 16 mL of dichloromethane. Treatment of this mixture with  $\text{NaN}_3$  (0.16mmol, 10.4mg) in methanol (2ml) afforded a green solution, which was magnetically stirred for 10 min and then filtered. Green block crystals were collected by filtration after slow evaporation of the resulting solution for several days. Yield: 60%. Anal. Calcd for  $\text{C}_{29}\text{H}_{28}\text{GdF}_{12}\text{N}_5\text{NiO}_{11}$ : C 32.66, H 2.65, N 6.56. Found: C 32.54, H 4.17, N 6.58. IR (KBr,  $\text{cm}^{-1}$ ): 2046 ( $\nu_{\text{N}_3^-}$ ), 1258, 1218, and 1147 ( $\nu_{\text{C-F}}$ ).

#### Preparation of $[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Tb}(\text{hfac})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (2)

Compound **2** was prepared as green block crystals in a similar method to that of **1**, except that  $\text{Tb}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  was used. Yield: 56%. Anal. Calcd for  $\text{C}_{29}\text{H}_{28}\text{TbF}_{12}\text{N}_5\text{NiO}_{11}$ : C 32.61, H 2.64, N 6.56. Found: C 32.53, H 2.65, N 6.58. IR (KBr,  $\text{cm}^{-1}$ ): 2047 ( $\nu_{\text{N}_3^-}$ ), 1255, 1218, and 1148 ( $\nu_{\text{C-F}}$ ).

#### Preparation of $[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Dy}(\text{hfac})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (3)

Compound **3** was prepared as green block crystals in a similar method to that of **1**, except that  $\text{Dy}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  was used. Yield: 58%. Anal. Calcd for  $\text{C}_{29}\text{H}_{28}\text{DyF}_{12}\text{N}_5\text{NiO}_{11}$ : C 32.50, H 2.63, N 6.53. Found: C 32.41, H 2.64, N 6.55. IR (KBr,  $\text{cm}^{-1}$ ): 2046 ( $\nu_{\text{N}_3^-}$ ), 1255, 1217, and 1147 ( $\nu_{\text{C-F}}$ ).

### X-ray Structure Determination.

The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 153 K. Cell parameters were retrieved using SMART software and refined using SAINT<sup>19</sup> on all observed reflections. Data was collected using a narrow-frame method with scan widths of  $0.30^\circ$  in  $\omega$  and an exposure time of 10 s/frame. The highly redundant data sets were reduced using SAINT<sup>19</sup> and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS<sup>20</sup> supplied by Bruker. Structures

were solved by direct methods using the program SHELXL-2013.<sup>21</sup> The positions of the metal atoms and their first coordination spheres were located from direct-methods *E* maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of  $U_{\text{iso}}$  which are tied 1.2 times or 1.5 times (for methyl- group) to the parent atoms.

**Table 1** Summary of crystallographic data for the complexes **1–3**

	<b>1</b>	<b>2</b>	<b>3</b>
formula	C <sub>29</sub> H <sub>28</sub> GdF <sub>12</sub> N <sub>5</sub> NiO <sub>11</sub>	C <sub>29</sub> H <sub>28</sub> TbF <sub>12</sub> N <sub>5</sub> NiO <sub>11</sub>	C <sub>29</sub> H <sub>28</sub> DyF <sub>12</sub> N <sub>5</sub> NiO <sub>11</sub>
fw	1066.52	1068.19	1071.77
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	18.351(3)	17.882(1)	17.852(2)
<i>b</i> , Å	10.868(2)	10.889(1)	10.661(1)
<i>c</i> , Å	19.911(3)	20.053(2)	19.936(1)
<i>a</i> , deg	90.00	90.00	90.00
<i>β</i> , deg	106.184(2)	106.038(2)	106.854(2)
<i>γ</i> , deg	90.00	90.00	90.00
<i>V</i> , Å <sup>3</sup>	3813.7(1)	3752.9(6)	3631.4(6)
<i>Z</i>	4	4	4
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.858	1.891	1.960
<i>T</i> / K	153	153	153
$\mu$ , mm <sup>-1</sup>	2.338	2.494	2.687
$\theta$ , deg	1.155 to 26.999	2.113 to 26.999	1.192 to 26.999
<i>F</i> (000)	2100.0	2104.0	2108.0
index ranges	-23 ≤ <i>h</i> ≤ 21 -13 ≤ <i>k</i> ≤ 13 -25 ≤ <i>l</i> ≤ 24	-22 ≤ <i>h</i> ≤ 21 -13 ≤ <i>k</i> ≤ 13 -25 ≤ <i>l</i> ≤ 24	-22 ≤ <i>h</i> ≤ 22 -13 ≤ <i>k</i> ≤ 13 -15 ≤ <i>l</i> ≤ 25
data/restraints /parameters	8330 / 10 / 534	8159 / 3 / 534	7911 / 1 / 534
GOF ( <i>F</i> <sup>2</sup> )	1.062	1.086	1.076
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0591 0.1517	0.0543 0.1330	0.0602 0.1500
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> , <i>wR</i> <sub>2</sub> <sup><i>b</i></sup> (all data)	0.0671 0.1527	0.0603 0.1336	0.0646 0.1512

$$R_1^a = \frac{\sum ||F_o| - |F_c||}{\sum F_o}, \quad wR_2^b = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Final crystallographic data and values of *R*<sub>1</sub> and *wR*<sub>2</sub> are listed in Table 1. Selected bond distances and angles for complexes **1–3** are listed in Tables S1–3. CCDC reference numbers 1046795 (**1**), 1046796 (**2**) and 1046794 (**3**).

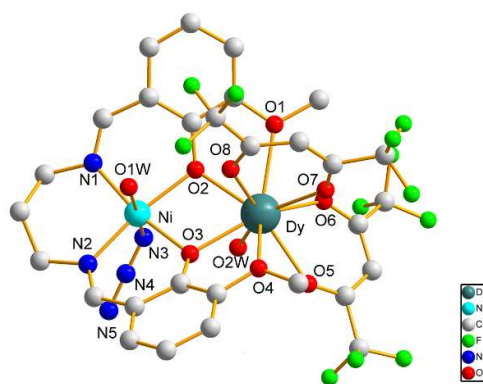
### Physical Measurements.

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. Infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400–4000  $\text{cm}^{-1}$  region. Magnetic susceptibilities for all polycrystalline samples were measured with the use of a Quantum Design MPMS-XL7 SQUID magnetometer in the temperature range 2.0–300 K. Field dependences of magnetization were measured using Quantum Design MPMS-XL5 SQUID system in an applied field up to 70 kOe.

## Results and discussion

### Structural Description.

Complexes **1–3** are isostructural, crystallize in the monoclinic space group of  $P2_1/c$ , and show similar structures.



**Figure 1.** Perspective drawing of the crystallographically structural unit of **3** showing the atom numbering. H atoms and one solvated water molecule are omitted for clarity.

As shown in Figure 1 and S1, the crystallographically independent unit contains one neutral Ni-Ln heterobinuclear unit,  $[\text{Ni}(\text{N}_3)(\text{H}_2\text{O})(\text{valpn})\text{Ln}(\text{hfac})_2(\text{H}_2\text{O})]$  ( $\text{Ln} = \text{Gd}$  for **1**,  $\text{Tb}$  for **2**,  $\text{Dy}$  for **3**, respectively), and one solvated water molecule. In all compounds, the Ni(II) ion situates in a slightly elongated octahedral surrounding with the equatorial plane occupied by two nitrogen and two phenoxo oxygen atoms arising from the inner compartment of the valpn ligand (Ni–O/N = 2.019(5)–2.040(4) Å for **1**, 2.000(5)–2.022(4) Å for **2**, and 1.994(5)–2.056(4) Å for **3**, respectively), whereas the axial positions are filled by an azido anion and one water molecule with the Ni–N distance of 2.074(6) Å for **1**, 2.285(6) Å for **2**, and 2.204(5) Å for **3**, and Ni–O distance of 2.125(4) Å for **1**, 2.211(4) Å for **2**, and 2.146(4) Å for **3**, respectively.

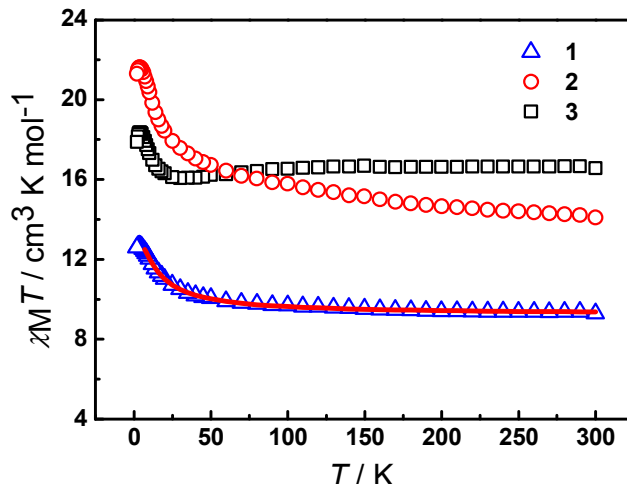
Each Ln(III) ion is nine-coordinated by outer four oxygen atoms from the valpn ligand and four oxygen atoms from two bidentate hfac anions, and the remaining one from a water molecule. The Ln–O distances fall in the range 2.336(4)–2.631(4) Å for **1**, 2.326(4)–2.593(4) Å for **2**, and 2.310(4)–2.615(4) Å for **3**, respectively, which indicate that these Ln(III) ions situate in a high degree of asymmetry. Concerning the coordination environment of the Ln(III) ions, by using the continuous shape measure theory and SHAPE software,<sup>22</sup> the best description would be the muffin ( $C_s$ ) with values of 0.70, 0.81, and 0.73 for **1–3**, respectively (table S4). In the heterodinuclear unit, the Ni(II) and Ln(III) ions are bridged to each other via two phenoxo oxygen atoms of the valpn ligand with the Ni···Ln distance of 3.491 Å for **1**, 3.490 Å for **2**, and 3.482 Å for **3**, respectively. The average bond angle of Ni–O–Ln is 105.44° for **1**, 106.36° for **2**, 105.53° for **3**, and the hinge angle (dihedral angle between the O–Ni–O and O–Ln–O planes) is 8.58° for **1**, 9.00° for **2**, 7.43° for **3**, respectively. The shortest intercluster M···M (Ni···Ni) distance is 6.207 Å for **1**, 6.106 Å for **2**, and 6.009 Å for **3**, respectively. The isolated cluster is connected through weak O–H···O, O–H···F, and O–H···N interactions between the solvated water molecules, the solvated water molecules and F atoms, and the solvated water molecules and the nonbridged azide groups, thus forming a 2D layer. The layers stack into a three-dimensional (3D) structure via Van der Waals' interactions (Figure S2).

## Magnetic Properties

### Static Magnetic Susceptibility.

The temperature dependence of magnetic susceptibilities for **1–3** was measured in the range of 2–300 K under an external magnetic field of 1000 Oe. For **1–3**, the temperature dependences of the  $\chi_M T$  product per Ni<sup>II</sup>Ln<sup>III</sup> unit are illustrated in Figure 2. For compound **1**, the  $\chi_M T$  value at room temperature is 9.29 cm<sup>3</sup> K mol<sup>-1</sup>, which is higher than the spin-only value of 8.88 cm<sup>3</sup> K mol<sup>-1</sup> for uncoupled Ni(II) and Gd(III) ions assuming  $g_{Ni} = g_{Gd} = 2$ . With decreasing the temperature, the  $\chi_M T$  value remains nearly constant until about 50 K, then increases sharply to a maximum value of 12.69 cm<sup>3</sup> K mol<sup>-1</sup> at 3.5 K, close to the value of 12.38 cm<sup>3</sup> K mol<sup>-1</sup> expected for an isolated  $S = 9/2$  spin resulting from ferromagnetic coupling between the Ni<sup>II</sup> ( $S = 1$ ) and Gd<sup>III</sup> ( $S = 7/2$ ) ions of **1**. Below this temperature,  $\chi_M T$  decreases, reaching 12.59 cm<sup>3</sup> K mol<sup>-1</sup> at 2.0 K, which may be ascribed to zero-field splitting (ZFS) and/or intercluster

antiferromagnetic interactions. The field dependence of the magnetizations recorded at 2 K (Figure 3) confirm the occurrence of ferromagnetic interactions between Ni(II) and Gd(III) ions with the magnetization value of  $9.29 N\beta$  at 7 T close to the expected value for Ni(II) and Gd(III) ions system with ferromagnetic interaction ( $S = 9/2$ ).



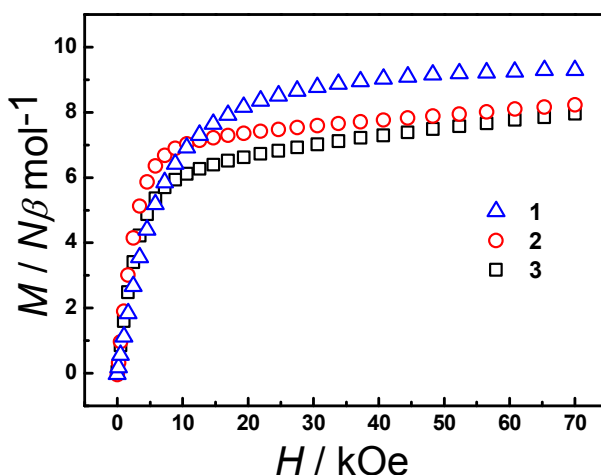
**Figure 2.** Temperature dependence of the  $\chi_M T$  product for **1-3** at 1 kOe.

The 7–300 K magnetic data were analyzed on the basis of the spin-only equation derived from a spin Hamiltonian  $\mathbf{H} = -J\mathbf{S}_{\text{Ni}} \cdot \mathbf{S}_{\text{Gd}}$ . The best fitting is obtained with  $g = 2.04$  and  $J = 2.58 \text{ cm}^{-1}$  ( $R = 9.8 \times 10^{-4}$ ). The positive  $J$  value is coincident with the intramolecular ferromagnetic interaction, which is very close to one reported by Andurh et al. for a dinuclear complex with the same ligand ( $2.3 \text{ cm}^{-1}$ ) and is in the range of  $\sim 0.2\text{--}5 \text{ cm}^{-1}$  for phenoxo-bridged NiGd complexes.<sup>18a,23</sup> It has been proved that the size of  $J$  is related to the dihedral angle defined by the ONiO and OGdO planes of the bridging network.<sup>23c</sup> The smaller dihedral angle, the larger  $J$ . The smaller ferromagnetic couplings may be due to the larger dihedral angle (OGdO, ONiO) of  $8.58^\circ$  for **1**.

The  $\chi_M T$  value of  $14.09 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K for **2** is slightly higher than the value of  $12.82 \text{ cm}^3 \text{ K mol}^{-1}$  expected for one Ni(II) ( $S = 1$ ,  $g = 2$ ) and one Tb(III) ( $J = 6$ ,  $g = 1.5$ ) magnetically isolated ions. On lowering the temperature, the  $\chi_M T$  value increases slowly at first, then rapidly to reach a maximum value of  $21.63 \text{ cm}^3 \text{ K mol}^{-1}$  at 4.0 K and then decreases abruptly. It seems that the effect of depopulation of the Stark sublevels of the Tb(III) ion is not pronounced.<sup>12c,16g</sup> The rapid increase of  $\chi_M T$  below 30 K supports the existence of a ferromagnetic exchange interaction between the Ni<sup>II</sup> and Tb<sup>III</sup> ions through diphenoxo bridges. Finally, the decrease of  $\chi_M T$  below



4.0 K is due to magnetic anisotropy effects and/or intercluster antiferromagnetic interactions. As shown in Figure 3, upon increasing the applied external magnetic field, the magnetization increases abruptly and linearly with field up to about 10 kOe, and then increases slowly to  $8.22 N\beta$  at 70 kOe, but does not reach the expected saturation value of  $11 N\beta$  ( $9 N\beta$  for Tb(III) ion and  $2 N\beta$  for Ni(II) ion) due to the crystal field effect on the Tb<sup>III</sup> ion. The sharp increase of  $M$  values at lower field indicates the presence of ferromagnetic couplings between Ni(II) and Tb(III) ions through the diphenoxo bridges.



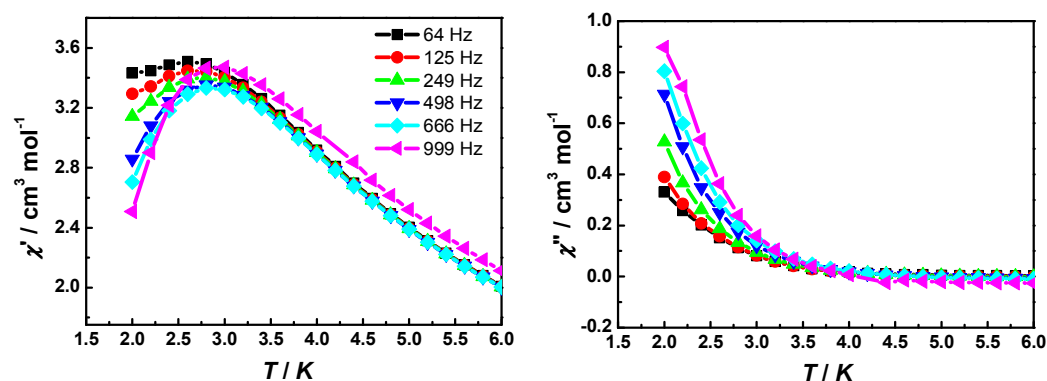
**Figure 3.** Field dependence of magnetization for **1-3** at 2.0 K.

The  $\chi_M T$  value of  $16.57 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K for **3** is slightly higher than the value of  $15.17 \text{ cm}^3 \text{ K mol}^{-1}$  expected for one Ni(II) ( $S=1$ ,  $g=2$ ) and one Dy(III) ( $J=15/2$ ,  $g=4/3$ ) magnetically isolated ions, and the  $\chi_M T$  value decreases gradually with decreasing temperature to  $16.06 \text{ cm}^3 \text{ K mol}^{-1}$  at 30.0 K. The slight decrease of  $\chi_M T$  is due to the depopulation of the Stark levels of the Dy(III) ion. Upon further cooling, the  $\chi_M T$  value rapidly increases to a maximum of  $18.36 \text{ cm}^3 \text{ K mol}^{-1}$  at  $\sim 4.0$  K. Below this temperature,  $\chi_M T$  drops abruptly, which may be ascribed to the presence of magnetic anisotropy and/or intercluster antiferromagnetic interactions. The increase of  $\chi_M T$  below 30 K is most likely due to the ferromagnetic interactions between Ni(II) and Dy(III) ions through the diphenoxo bridges, which is supported in view of the magneto-structural studies carried out for other systems containing this bridging pathway.<sup>18a,23,24</sup> The magnetizations of **3** from zero dc field to 70 kOe at 2.0 K are also shown Figure 3. The initial magnetization increases abruptly and linearly with field up to about 10 kOe, and then increases slowly to  $7.95 N\beta$  at 70 kOe, but does not

reach the expected saturation value of  $12 N\beta$  ( $10 N\beta$  for Dy(III) ion and  $2 N\beta$  for Ni(II) ion), due to the crystal field effect on the Dy(III) ion. The rapid increase of the magnetization in the region of low applied fields supports the occurrence of ferromagnetic couplings between Ni(II) and Dy(III) ions through the diphenoxo bridges.

### Dynamic Magnetic Properties.

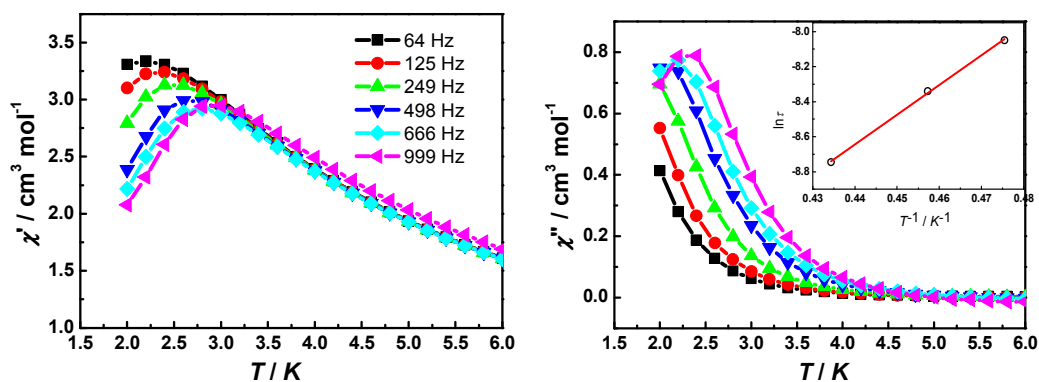
Ac magnetic susceptibility studies were performed for compounds **2** and **3** in the 2–10 K temperature range in a zero applied dc field and a 2 Oe ac field oscillating at 1000 Hz to investigate the dynamics of the magnetization. There was no signal in the out-of-phase ( $\chi''$ ) down to 2 K for **2** and a weak  $\chi''$  signal was observed at temperatures down to 3.0 K for **3** (Figure S3), which may be due to the presence of fast quantum tunneling of magnetization slowed down by a applied dc field.<sup>25</sup>



**Figure 4.** Temperature dependence of the in-phase  $\chi'$  and out-of-phase  $\chi''$  at different frequencies in a 2 Oe ac field oscillating at 64–999 Hz with a dc field of 1 KOe for **2**.

Under a 1000 Oe dc field, compound **2** exhibited a frequency-dependent  $\chi''$  signal below 4 K (Figure 4). Unfortunately, no peaks were found at frequencies lower than 1000 Hz until 2.0 K, which impeded confirmation of SMM-type behavior. For **3**, several peaks in the out-of-phase ac susceptibility are observed under a 1000 Oe dc field for higher frequencies and display strongly frequency-dependent indicative of the onset of slow magnetic relaxation (Figure 5). To rule out the presence of glassiness, a quantitative measure of the frequency dependence was estimated with the frequency shift parameter first introduced by Mydosh.<sup>26</sup> The peak temperatures of in-of-phase ( $\chi'$ ) can be measured by the parameter  $\varphi = (\Delta T_p/T_p)/\Delta(\log f) = 0.28$ , which is in excellent agreement with that expected for superparamagnetic behavior ( $0.1 \leq \varphi$

$\leq 0.3)^{1-6}$ . The relaxation time  $\tau$  obtained from the  $\chi''(T)$  peaks obeys the Arrhenius equation with physically reasonable parameters ( $\Delta\tau/k_B = 16.9$  K and  $\tau_0 = 1.02 \times 10^{-7}$  s), which is located in the normal range for SMMs (Figure 5, inset).



**Figure 5.** Temperature dependence of the in-phase  $\chi'$  and out-of-phase  $\chi''$  at different frequencies in a 2 Oe ac field oscillating at 64–999 Hz with a dc field of 1 KOe for **3**. The inset is the Arrhenius fit for the  $\ln \tau$  vs  $T^{-1}$  plot. The red solid line represents the best fits of the data.

It is worth mentioning that the dynamic magnetic behavior of **3** is different from that in the related NiDy heterodinuclear compound ( $[\text{Ni}(\text{CH}_3\text{CN})(\text{H}_2\text{O})(\text{valpn})\text{Dy}(\text{NO}_3)(\text{H}_2\text{O})_3] \cdot 2\text{NO}_3 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ ).<sup>18a</sup> Indeed, the NiDy compound is ferromagnetically coupled and shows a slow magnetic relaxation of magnetization. But only a maximum for the  $\chi''$  is observed above 2 K for the highest frequency investigated, 1490 Hz. As a result, the conclusion that the NiDy compound displays a SMM behavior can not be drawn. While compound **3** has been proved to display a SMM behavior. The NiDy compound and **3** have similar structures (The Dy(III) ions are nine-coordinated in both compounds. The Ni...Dy distance is 3.466 and 3.482 Å, and the dihedral angle between the O–Ni–O and O–Dy–O planes is 6.15 and 7.43° for the NiDy compound and **3**, respectively), but the DyO<sub>9</sub> coordination spheres determined by the ligand fields are different. The Dy(III) ion lies in the muffin ( $C_s$ ) for **3**, however, between the spherical capped square antiprism ( $C_{4v}$ ) and spherical tricapped trigonal prism ( $D_{3h}$ ) for the NiDy compound. It is well-known that the magnetic anisotropy of an exchange-coupled system is related to the individual anisotropies of the metal ions and the relative orientation of all single-ion easy axes within the molecule.<sup>27</sup> The anisotropy of each metal ion depends on the coordination configurations and the corresponding ligand field. So the different ligand field around the Dy(III) ion within the NiDy compound and **3** is mostly responsible

for the different relaxation dynamics observed.

## Conclusion

By using the  $\text{N}_3^-$ , hexafluoroacetylacetonato anions and compartmental Schiff-base ligand, three new Ni-Ln heterodinuclear compounds have been prepared and structurally characterized. The Dy derivate exhibits field-induced single-molecule magnet behavior with effective energy barrier of 16.9 K under an 1000 Oe dc field. Here, the azide anion, not as we expected, connect the heterodinuclear unit to form larger clusters or one-dimensional chain, which may be ascribe to the effect of steric hindrance of hexafluoroacetylacetonato anions and/or the restrictions of reaction conditions such as reaction time and/or temperature. In our further work, we will try to obtain  $\text{N}_3^-$ -bridged Ni-Ln compounds exhibiting single-molecule/single-chain magnets behaviors by regulating ligand fields and/or changing reaction conditions.

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## Supporting Information

Additional structure and magnetic characterization data, and X-ray crystallographic files in CIF format for **1–3**.

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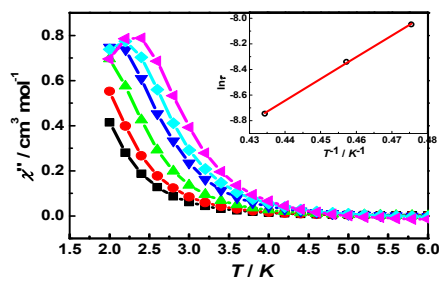


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## GRAPHIC ABSTRACT

**Synopsis**

Three isomorphous Ni-Ln heterodinuclear complexes were synthesized and structurally characterized. The Dy derivative exhibits field-induced single-molecule magnet behavior with effective energy barrier of 16.9 K under the 1000 Oe dc field.