

# Diphenoxo-Bridged Ni<sup>II</sup>Ln<sup>III</sup> Dinuclear Complexes as Platforms for Heterotrimetallic (Ln<sup>III</sup>Ni<sup>II</sup>)<sub>2</sub>Ru<sup>III</sup> Systems with a High-Magnetic-Moment Ground State: Synthesis, Structure, and Magnetic Properties

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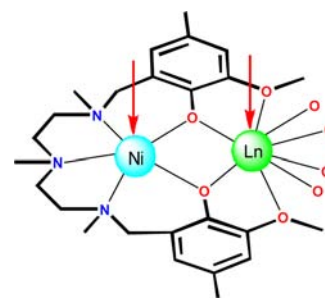
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## Supporting Information

**ABSTRACT:** The first examples of pentanuclear heterotrimetallic [(LnNi)<sub>2</sub>Ru] [Ln<sup>3+</sup> = Gd (1) and Dy (2)] complexes were prepared and magnetostructurally characterized. They exhibit ferromagnetic interactions, leading to a high-magnetic-moment ground state.

In recent years, there has been a growing interest in studying the magnetic properties of discrete 3d/4f metal aggregates because they can behave as single-molecule magnets (SMMs).<sup>1</sup> These chemically and physically fascinating nanomagnets retain a magnetic moment after removal of an applied magnetic field.<sup>2</sup> The SMM behavior is due to the existence of an energy barrier that prevents reversal of the molecular magnetization and causes slow relaxation of magnetization at low temperature. This energy barrier depends on the large-spin multiplicity of the ground state ( $S_T$ ) and the easy-axis (or Ising-type) magnetic anisotropy of the entire molecule. The incorporation of heavy lanthanide ions, such as Tb<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup>, and Er<sup>III</sup>, in 3d–4f cluster complexes is a sensible strategy for the design of SMMs not only because they have large angular and magnetic moments in the multiplet ground state as a consequence of strong spin–orbit coupling but also because these metal ions are assumed to possess a large Ising-type magnetic anisotropy.<sup>1</sup> Moreover, the magnetic coupling of the heavy lanthanide ions with 3d transition-metal ions is often ferromagnetic, which leads to ground states with even larger magnetic moments.<sup>1</sup> In principle, a reasonable strategy to obtain new discrete molecular species with improved SMM properties could be that of assembling 3d–4f dinuclear complexes exhibiting latent SMM behavior with anisotropic paramagnetic metalloligands. It should be noted that this strategy has been successfully applied during the past few years by Andruh to obtain a number of trimetallic 3d–3d'–4f and 3d–4f–4d complexes.<sup>1d</sup> However, the majority of these systems exhibit nondiscrete 1D to 3D molecular structures. Recently, we have reported two new nickel–dysprosium complexes exhibiting SMM behavior<sup>3a</sup> with a new non-Schiff base compartmental ligand [H<sub>2</sub>L = *N,N',N''*-trimethyl-*N,N''*-bis(2-hydroxy-3-methoxy-5-methylbenzyl)-diethylenetriamine; see Figure 1] that contains an N<sub>3</sub>O<sub>2</sub> pentacoordinated inner site that forces the Ni<sup>II</sup> ion to saturate its coordination sphere with a donor atom (Figure 1). If this



**Figure 1.** Coordination ability of the L<sup>2-</sup> ligand and free available coordination positions on the Ni<sup>2+</sup> and Ln<sup>3+</sup> ions (red arrows).

atom belongs to a paramagnetic metalloligand, then discrete trimetallic species with interesting magnetic properties could be obtained.

Among metalloligands, cyanometallates occupy a prevalent place because they have been shown to be very effective in mediating magnetic exchange interactions.<sup>4</sup> It has been recently shown that the anisotropic [Ru<sup>III</sup>(acac)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> metalloligand is able to afford cyano-bridged Ru<sup>III</sup>M<sup>II</sup> (M<sup>II</sup> = Mn, Co, and Ni) and Ru<sup>III</sup>Ln<sup>III</sup> complexes with interesting magnetic properties, the Ru<sup>III</sup>–Ni<sup>II</sup> systems exhibiting ferromagnetic interactions.<sup>5</sup> In view of this, we decided to assemble [Ni(μ-L)Ln(NO<sub>3</sub>)<sub>3</sub>]<sup>+</sup> cationic units and the anisotropic [Ru<sup>III</sup>(acac)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> anionic metalloligand with the aim of obtaining discrete trimetallic (Ln<sup>III</sup>Ni<sup>II</sup>)Ru<sup>III</sup> species with enhanced magnetic anisotropy and magnetic moments in the ground state and eventually SMM behavior.

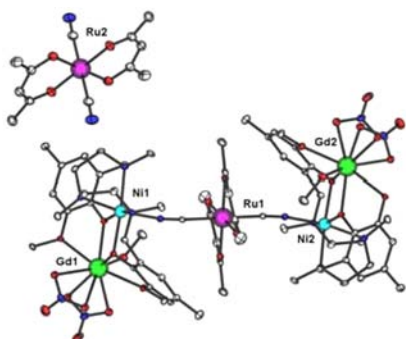
We report here the synthesis, structures, and magnetic properties of two pentanuclear heterotrimetallic complexes, [{Ru(acac)<sub>2</sub>(μ-CN)<sub>2</sub>}{Ni(μ-L)Ln((CH<sub>3</sub>OH)(NO<sub>3</sub>)<sub>2</sub>)<sub>2</sub>}[Ru(acac)<sub>2</sub>(CN)<sub>2</sub>]<sub>2</sub>·4CH<sub>3</sub>OH [Ln<sup>III</sup> = Gd (1) and Dy (2)]. These compounds were prepared [see the Supporting Information (SI) for details] by reacting a green methanolic solution of the corresponding nickel–lanthanide complex [formed in situ from the reaction of H<sub>2</sub>L with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and subsequently with Ln(NO<sub>3</sub>)<sub>3</sub>·*n*H<sub>2</sub>O in methanol and using a 1:1:1 molar ratio] and *trans*-Ph<sub>4</sub>P[Ru(acac)<sub>2</sub>(CN)<sub>2</sub>] in a 1:1 molar ratio.

Received: April 25, 2012

Published: June 19, 2012



Because complexes **1** and **2** are isostructural, only the structure of **1** will be described in detail (crystallographic data and selected bond lengths and angles are given in Tables S1 and S2 in the SI). It consists of S-shaped centrosymmetric pentanuclear  $[\{\text{Ru}(\text{acac})_2(\mu\text{-CN})_2\}\{\text{Ni}(\mu\text{-L})\text{Gd}((\text{CH}_3\text{OH})(\text{NO}_3)_2)_2\}]^+$  cations, centrosymmetric *trans*- $[\text{Ru}(\text{acac})_2(\text{CN})_2]$  anions, and four methanol molecules of crystallization (Figure 2), linked together by hydrogen bonds (Figure S1 and Table S4



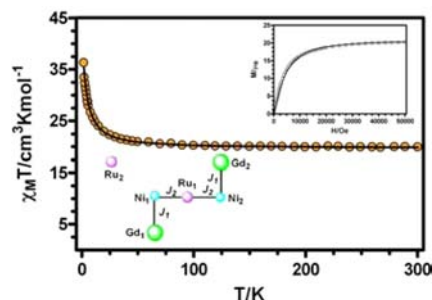
**Figure 2.** Perspective view of the structure of **1**. Color code: C, gray; N, blue; O, red; Ni, light blue; Gd, green; Ru, violet. Hydrogen atoms and methanol crystallization molecules have been omitted for the sake of clarity.

in the SI). Within each pentanuclear  $[(\text{NiGd})_2\text{Ru}]^+$  cationic unit, two dinuclear cationic fragments  $[\text{Ni}(\mu\text{-L})\text{Gd}(\text{CH}_3\text{OH})(\text{NO}_3)_2]^+$ , in which the  $\text{Ln}^{\text{III}}$  and  $\text{Ni}^{\text{II}}$  ions are bridged by two phenoxo groups of the  $\text{L}^{2-}$  ligand, are connected at the  $\text{Ni}^{\text{II}}$  ions by the linear *trans*- $[\text{Ru}(\text{acac})_2(\text{CN})_2]^-$  metalloligand.

As was previously observed for other nickel–lanthanide complexes<sup>3</sup> bearing the  $\text{L}^{2-}$  ligand, inside the  $[\text{Ni}(\mu\text{-L})\text{Gd}(\text{CH}_3\text{OH})(\text{NO}_3)_2]^+$  fragments, the  $\text{L}^{2-}$  ligand wraps around the  $\text{Ni}^{\text{II}}$  ions in such a way that the three amine nitrogen atoms occupy *fac* positions on the slightly distorted octahedral  $\text{NiN}_4\text{O}_2$  coordination polyhedron (see Table S3 in the SI for continuous shape measures), with Ni–N distances of  $\approx 2.15$  Å, which are  $\approx 0.1$  Å longer than the Ni–N<sub>cyanide</sub> and Ni–O<sub>phenoxo</sub> bond distances. The  $\text{Ln}^{\text{III}}$  ion exhibits a  $\text{GdO}_9$  coordination sphere, consisting of the two phenoxo bridging oxygen atoms, the two methoxy oxygen atoms, one oxygen atom from a coordinated methanol molecule, and four oxygen atoms belonging to two bidentate nitrate anions. The  $\text{GdO}_9$  coordination sphere is rather asymmetric, exhibiting Ln–O bond distances in the range of 2.3–2.6 Å. In fact, the  $\text{GdO}_9$  coordination sphere can be considered as an intermediate between various nine-vertex coordination polyhedra (see Table S3 in the SI). As expected, the bridging fragment is rather unsymmetrical, with Ni–O<sub>phenoxo</sub> and Gd–O<sub>phenoxo</sub> bond distances of  $\approx 2.0$  and  $\approx 2.3$  Å, respectively, and almost planar, with a hinge angle (dihedral angle between the O–Ni–O and O–Gd–O bridging angles) of  $5.3^\circ$  and Ni–O–Gd bridging angles of  $109.5^\circ$  and  $108.4^\circ$ . The Ru–CN–Ni bridging fragment is slightly bent with Ru–C–N and C–N–Ni angles of  $175.5^\circ$  and  $172.3^\circ$ , respectively, whereas the Ru–C and Ni–N bond distances are 2.077 and 2.056 Å, respectively.

The intramolecular Ni $\cdots$ Ru, Ni $\cdots$ Gd, and Ru–Ni distances are 5.251, 3.575, and 6.468 Å, respectively, whereas the Ni–N–C–Ru fragment is quite linear and the shortest intermolecular Ru $\cdots$ Ru, Ru $\cdots$ Gd, Ru $\cdots$ Ni, Gd $\cdots$ Gd, and Ni $\cdots$ Ni distances are 8.882, 8.929, 7.296, 8.626, and 8.565 Å. The temperature dependences of  $\chi_{\text{M}}T$  for complexes **1** and **2** ( $\chi_{\text{M}}$  is the molar

magnetic susceptibility) are displayed in Figures 3 and S2 in the SI, respectively. Let us to start with the  $(\text{NiGd})_2\text{Ru}$  complex **1**, whose magnetic properties are easier to analyze.



**Figure 3.** Temperature dependence of the  $\chi_{\text{M}}T$  product at 1000 Oe for **1**. Inset: Field dependence of the magnetization at 2 K. Solid lines show the best fits with the parameters indicated in the text.

At room temperature, the  $\chi_{\text{M}}T$  value for **1** of  $19.84 \text{ cm}^3 \text{ K mol}^{-1}$  is larger than the expected value for a set of two  $\text{Ni}^{2+}$  ( $S = 1$ ), two  $\text{Gd}^{3+}$  ( $S = 7/2$ ), and two  $\text{Ru}^{2+}$  ( $S = 1/2$ ) magnetically isolated ions ( $18.92 \text{ cm}^3 \text{ K mol}^{-1}$  with  $g_{\text{Ni}} = g_{\text{Ru}} = 2.15$  and  $g_{\text{Gd}} = 2.0$ , the usual values for these ions), which may be due to the orbital contribution of the low-spin  $\text{Ru}^{\text{III}}$  ion with an octahedral geometry and a  $^2T_{2g}$  ground-state term. On a decrease in the temperature,  $\chi_{\text{M}}T$  for **1** first slightly increases from 300 to 40 K and then increases sharply to  $36.23 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K, thus indicating the existence of a ferromagnetic interaction between the  $\text{Ni}^{\text{II}}$  and  $\text{Gd}^{\text{III}}$  ions and between the  $\text{Ni}^{\text{II}}$  and  $\text{Ru}^{\text{III}}$  ions in the pentanuclear  $(\text{Ni}_2\text{Gd}_2)\text{Ru}$  cationic unit, giving rise to a  $S = 19/2$  ground state.

The  $M$  vs  $H$  plot at 2 K (see the inset in Figure 3) shows a rapid increase in the magnetization at low field in accord with a high-spin ground state for this complex and a rapid saturation that is almost complete at 4 T, reaching a value of  $20.21 \text{ N}\mu_{\text{B}}$ . This value agrees well with that expected for a ferromagnetically coupled  $(\text{Ni}_2\text{Gd}_2)\text{Ru}$  unit with  $S = 19/2$  plus an isolated low-spin  $\text{Ru}^{\text{III}}$  ion ( $M_s = 20.07 \text{ N}\mu_{\text{B}}$  with  $g_{\text{Ru}} = 2.15$ ).

The magnetic data were analyzed by using the following isotropic Hamiltonian (see the inset in Figure 3):

$$H = -J_1(S_{\text{Gd1}}S_{\text{Ni1}} + S_{\text{Gd2}}S_{\text{Ni2}}) - J_2(S_{\text{Ni1}}S_{\text{Ru1}} + S_{\text{Ni2}}S_{\text{Ru1}})$$

This Hamiltonian was numerically diagonalized by using the *MAGPACK* program.<sup>6</sup> The  $\chi_{\text{M}}T$  value for the  $[\text{Ru}(\text{acac})_2(\text{CN})_2]^-$  counteranion was calculated from the Curie law using the  $g$  value reported in the literature ( $g = 2.15$ ) for this anion.<sup>5</sup> In order to avoid overparametrization, an average  $g$  value was considered for the whole pentanuclear unit and the local anisotropy of the  $\text{Ni}^{2+}$  ions was not taken into account (the  $M$  vs  $H/T$  plot given in Figure S3 in the SI clearly shows the absence of significant anisotropy in **1** because the data are superposed on a single master curve). The best-fit parameters were  $J_1 = +1.86 \text{ cm}^{-1}$ ,  $J_2 = +3.02 \text{ cm}^{-1}$ , and  $g_{\text{av}} = 2.06$  with  $R = 2.1 \times 10^{-7}$ . The calculated  $M(H)$  curve at 2 K, using these  $J$  parameters with  $g_{\text{Gd}} = 2.00$ ,  $g_{\text{Ni}} = 2.15$ , and  $g_{\text{Ru}} = 2.15$  and calculating the magnetization for the  $[\text{Ru}(\text{acac})_2(\text{CN})_2]^-$  counteranion from the Brillouin function, reproduces quite well the experimental magnetization data (see the inset in Figure 3). Density functional theory (DFT)-calculated values were  $J_1 = +3.5 \text{ cm}^{-1}$  and  $J_2 = +6.1 \text{ cm}^{-1}$  (see the SI for details).

Experimental results and DFT calculations carried out by us and others on di- $\mu$ -phenoxo  $\text{Gd}-(\text{O})_2\text{-Ni}$  complexes<sup>3</sup> indicate

that the ferromagnetic interaction between the Ni<sup>2+</sup> and Gd<sup>3+</sup> ions increases with the planarity of the N–O<sub>2</sub>–Gd fragment and with an increase of the Ni–O–Gd angle ( $\theta$ ). Taking into account this magnetostructural correlation, the experimental  $J_{\text{NiGd}}$  value for **1** ( $J = +1.87 \text{ cm}^{-1}$ ) is not unexpected because it exhibits a large  $\theta$  angle (average value of  $108.95^\circ$ ) and is almost planar with a low hinge angle of  $5.3^\circ$ . In fact, the  $J$  value for **1** is slightly smaller than that observed for the dinuclear planar complex  $[\text{Ni}(\text{H}_2\text{O})(\mu\text{-L})\text{Gd}(\text{NO}_3)_3] \cdot 2\text{CH}_3\text{OH}$  ( $J = +2.16 \text{ cm}^{-1}$ ), which contains the same L<sup>2-</sup> bridging ligand as **1** and exhibits  $\theta$  and hinge angles of  $109.4^\circ$  and  $2.3^\circ$ , respectively.<sup>3b</sup> As far as the  $J_2$  parameter is concerned, assuming octahedral geometries, its ferromagnetic nature can be justified by the  $\sigma/\pi$  orthogonality of the magnetic orbitals on the low-spin Ru<sup>3+</sup> ( $t_{2g}$   $\pi$  in nature) and Ni<sup>2+</sup> ( $e_g$   $\sigma$  in nature) metal ions. In good agreement with this are the five reported examples of Ni<sup>II</sup>–Ru<sup>III</sup> complexes containing a  $[\text{Ru}(\text{acac})_2(\text{CN})_2]^-$  bridging group connecting the Ru<sup>3+</sup> and Ni<sup>2+</sup> ions, which exhibit ferromagnetic interactions with  $J$  values between  $+1.70$  and  $+6.6 \text{ cm}^{-1}$ .<sup>5b,d,e</sup> The differences in the magnitude of  $J_{\text{NiRu}}$  for all of these compounds are more likely due to subtle structure differences in their nickel coordination polyhedra (set of coordinating atoms and distortion), whereas the small magnitude of the ferromagnetic interaction is due to the unfavorable orientation of the magnetic orbitals of the low-spin Ru<sup>3+</sup> ion and Ni<sup>2+</sup> ions.<sup>5d</sup>

The  $\chi_{\text{M}}T$  value of  $29.28 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K for **2** (Figure S2 in the SI) is compatible with the calculated value of  $31.10 \text{ cm}^3 \text{ K mol}^{-1}$  for a set of two Ni<sup>II</sup> ( $S = 1; g = 2.15$ ), two Ru<sup>III</sup> ( $S = 1/2, g = 2.15$ ), and two Dy<sup>III</sup> ( $4f^9, J = 15/2, S = 5/2, L = 5$ , and  $^6H_{15/2}$ ) in the free-ion approximation, considered as magnetically independent centers. The  $\chi_{\text{M}}T$  value decreases slowly with decreasing temperature to a minimum value of  $27.45 \text{ cm}^3 \text{ K mol}^{-1}$  at 40.0 K and then increases at lower temperatures, reaching a maximum value of  $32.21 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. The decrease of the  $\chi_{\text{M}}T$  product between 300 and 25 K is due to depopulation of the Stark levels of the dysprosium, whereas the increase of  $\chi_{\text{M}}T$  below 40 K is likely to be due to a ferromagnetic interaction between Ni<sup>II</sup> and Dy<sup>III</sup> and between Ni<sup>II</sup> and Ru<sup>III</sup>. Both ferromagnetic interactions are not unexpected in view of the results obtained for compound **1** and for  $\{\text{Ni}(\mu\text{-L})\text{Dy}(\mu\text{-X})(\text{NO}_3)_2\}_2$  ( $X = \text{acetate, benzoate, and nitrate}$ ) dinuclear complexes, which always exhibited ferromagnetic interactions between Ni<sup>2+</sup> and Dy<sup>3+</sup> metal centers. Alternating-current (ac) dynamic susceptibility measurements were performed on complexes **1** and **2** in order to know whether or not they exhibit SMM behavior. As expected, compound **1** does not show any out-of-phase ( $\chi''$ ) component of ac susceptibility. However, compound **2** exhibits frequency dependence of the in-phase ( $\chi'$ ) and out-of-phase signals and, therefore, slow relaxation of magnetization typical for a SMM but without showing any maximum in  $\chi''$  above 2 K at frequencies reaching 1400 Hz (Figure S4 in the SI). These results show once again that the introduction of several anisotropic ions, such as Ni<sup>II</sup>, Ln<sup>III</sup>, and Ru<sup>III</sup> in compound **1**, does not guarantee a larger uniaxial anisotropy because the local anisotropies can be combined in a subtractive manner. This possible subtractive effect, together with the very weak  $J_{\text{NiLn}}$  and  $J_{\text{NiRu}}$  coupling constants, could promote smaller values of the energy barrier.

In conclusion, we have successfully obtained for the first time heterotrimetallic (Ln<sup>III</sup>Ni<sup>II</sup>)Ru<sup>III</sup> complexes using the strategy of assembling the  $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{CN})_2]^-$  anionic metalloligand and

$[\text{Ni}(\mu\text{-L})\text{Ln}(\text{NO}_3)_3]^+$  cationic units, in which the Ni<sup>II</sup> ion has an available coordination position for the nitrogen-donor atom of the cyanide bridging group. The new pentanuclear  $[(\text{LnNi})_2\text{Ru}]^+$  complexes (Ln<sup>3+</sup> = Gd and Dy) exhibit ferromagnetic interactions between the Ni<sup>2+</sup> and Ln<sup>3+</sup> ions as well as between the Ni<sup>2+</sup> and Ru<sup>3+</sup> ions, leading, in the case of **1**, to an  $S = 19/2$  spin ground state. Compound **2** seems to exhibit slow relaxation of magnetization but without reaching any maximum in the temperature dependence of the out-of-phase susceptibility above 2 K. We are now pursuing the preparation of new examples of trimetallic complexes by assembling other  $[\text{M}(\mu\text{-L})\text{Ln}(\text{NO}_3)_3]^+$  cationic units ( $\text{M}^{2+} = \text{Mn}$  and  $\text{Co}$ ) with other metalloligands. Work along this line is in progress.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

X-ray crystallographic data in CIF format, synthetic procedures, crystallographic, and magnetic data. 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.

## ■ ACKNOWLEDGMENTS

This work was supported by the MEC (Spain; Projects CTQ-2008-02269/BQU and CTQ2011-24478), the Junta de Andalucía (FQM-195 and Project of Excellence P08-FQM-03705), and the University of Granada.

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