

# Unprecedented Nitronyl Nitroxide Bridged 3d–4f Complexes: Structure and Magnetic Properties

Mei Zhu, Yun-Gai Li, Yue Ma, Li-Cun Li,\* and Dai-Zheng Liao

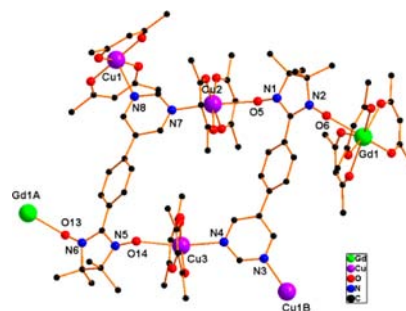
Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry and Tianjin Key Laboratory of Metal and Molecule-based Material Chemistry, Nankai University, Tianjin 300071, China

## Supporting Information

**ABSTRACT:** Two novel 2p–3d–4f compounds,  $\{Ln(hfac)_3[Cu(hfac)_2]_3(NITPhPyrim)_2\}$  [ $Ln = Gd$  (1),  $Dy$  (2)], have been obtained by reacting phenyl pyrimidyl nitronyl nitroxide with  $Cu(hfac)_2$  and  $Ln(hfac)_3$ . These two compounds are the first examples of two-dimensional 3d–4f complexes bridged by nitronyl nitroxide radicals. Overall ferromagnetic behaviors were observed in both compounds.

Heterospin systems have received intense interest in the field of molecular magnetism.<sup>1</sup> Such systems represent one particularly promising strategy for the design of molecular magnetic materials such as high  $T_C$  molecular-based magnets,<sup>2</sup> multifunctional materials,<sup>3</sup> and single-chain magnets.<sup>4</sup> Most reported heterospin systems so far are constructed from two different spin carriers such as 3d–3d',<sup>5</sup> 3d–4f,<sup>6</sup> 3d–4f',<sup>7</sup> 2p–3d,<sup>8</sup> and 2p–4f.<sup>9</sup> In contrast, very few heterospin compounds containing three different spin carriers have been obtained owing to the synthetic challenges inherent in their creation,<sup>10</sup> and only two examples with three different types of spin carriers, 2p–3d–4f<sup>11</sup> and 3p–3d–4f,<sup>12</sup> were reported recently. On the other hand, nitronyl nitroxide radicals can directly bind metal ions not only to generate heterospin compounds but also to produce the strongest possible magnetic coupling. Most of nitronyl nitroxide metal compounds reported to date are based on 3d or 4f metal ions having zero- and one-dimensional (1D) structure,<sup>8a,9</sup> while the nitronyl nitroxide radical bridged 3d–4f complexes have not been reported. According to the soft–hard principle, the lanthanide ions are hard acids; thus, they prefer O rather than N donor atoms, while 3d metal ions, as borderline acids, have a strong affinity with N and O donor atoms.<sup>13</sup> Thus, in order to combine 3d and 4f ions within one system, we use a 2-[4-(5-pyrimidyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITPhPyrim) radical ligand containing N and O donor atoms to build 3d–4f complexes. Noticeably, 3d-rad or 4f-rad complexes have been obtained by using nitronyl nitroxide radicals with N donor atoms.<sup>14</sup> In this communication, we report on the synthesis, crystal structure, and magnetic properties of two novel two-dimensional (2D) compounds,  $\{Ln(hfac)_3[Cu(hfac)_2]_3(NITPhPyrim)_2\}$  [ $Ln = Gd$  (1),  $Dy$  (2); hfac = hexafluoroacetylacetonate], which contain three different types of spin carriers: a nitronyl nitroxide radical (2p), a 3d metal ion ( $Cu^{2+}$ ), and a rare earth ion, 4f ( $Gd^{3+}$  or  $Dy^{3+}$ ). To our knowledge, they are the first reported 2D 2p–3d–4f compounds in which a nitronyl nitroxide radical acts as a bridging ligand.

Reaction of the NITPhPyrim radical (0.02 mmol) with  $Ln(hfac)_3$  (0.01 mmol) ( $Ln^{III} = Gd, Dy$ ), followed by reaction with  $Cu(hfac)_2$  (0.03 mmol) in heptane, affords green crystals of 1 and 2, respectively. X-ray crystallography shows that complexes 1 and 2 are isomorphous. Therefore, only the structure of complex 1 will be described. Complex 1 is a 2D coordination polymer built up by  $Cu(hfac)_2$  and  $Gd(hfac)_3$  units bridged by NITPhPyrim radicals via their nitroxide groups and pyrimidine rings. There are three crystallographically independent Cu atoms and one independent Gd atom in the asymmetric unit (Figure 1).



**Figure 1.** Asymmetric unit found in 1. H and F atoms are not shown for the sake of clarity. Symmetry code: A,  $x, -1/2 - y, -z + 1$ ; B,  $x - 1, y, z$ .

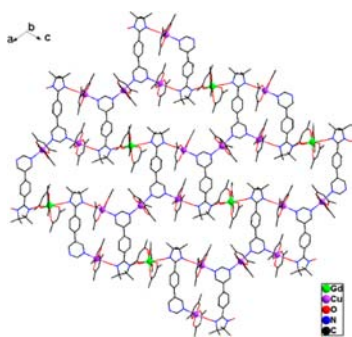
Cu1 is coordinated by two N atoms in axial positions from two pyrimidine rings of two NITPhPyrim radical ligands and completed to six by four O atoms in the equatorial plane from two didentate hfac ligands. Cu2 and Cu3 exhibit similar coordination environments, coordinated by four O atoms in the equatorial plane from two hfac units, one pyrimidine nitrogen from a NITPhPyrim radical, and one O atom from the NO group provided by the other NITPhPyrim radical ligand. The average equatorial Cu–O (hfac) bond distance is 1.941 Å, while the apical Cu–O (radical) bond lengths are 2.449(5) Å for Cu2–O5 and 2.527(5) Å for Cu3–O14 and the axial Cu–N bond lengths range from 2.264(6) to 2.448(7) Å, which are significantly longer than the basal bond lengths because of the Jahn–Teller effect.<sup>15</sup> The Gd atom is octacoordinated with two O atoms from two NO groups of two NITPhPyrim radicals and six O atoms from three hfac units. The Gd–O (radical) distances are 2.355(5) and 2.345(5) Å for Gd1–O6 and Gd1–O13#1 (#1:  $x, -y - 1/2, z + 1/2$ ), respectively, which compare well with those of the reported  $Ln(hfac)_3$ –nitronyl nitroxide complexes.<sup>16</sup> As shown in Figure

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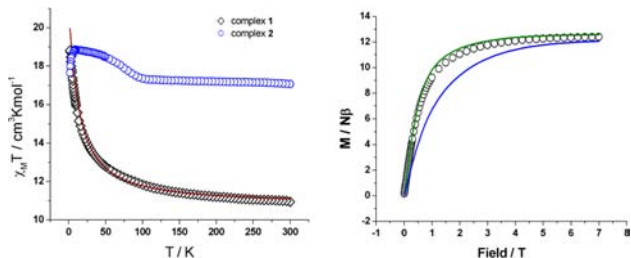
S1 (Supporting Information, SI), two Cu atoms (Cu2 and Cu3) are connected by two NITPhPyrim radical ligands through two nitroxide groups and two pyrimidine N atoms to form a cyclic dimer, and each dimer unit acts as a bidentate ligand to bind to two Gd atoms through its two NO groups to produce a 1D chain along the *c* axis. Then, these 1D chains are connected to the Cu atoms (Cu1) through the pyrimidine N atoms to result in a 2D heterospin layer. The compound has a unique topological architecture type that consists of a 2D network with alternating cyclic  $[\text{Cu}_2(\text{NITPhPyrim})_2]$  dimer rings and rectangle-like  $[\text{Cu}_4\text{Gd}_2]$  rings (Figure 2), in which the NITPhPrim radical



**Figure 2.** 2D layer structure of complex 1. H and F atoms are not shown for the sake of clarity.

ligand acts as tetradentate to bridge metal ions in  $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$  mode. In the cyclic  $[\text{Cu}_2(\text{NITPhPyrim})_2]$  dimer, the distance of two  $\text{Cu}^{\text{II}}$  ions is 8.140 Å. For a rectangle-like  $[\text{Cu}_4\text{Gd}_2]$  ring, two NITPhPyrim radical ligands behave as the two shorter edges and the longer edge is formed by one Gd atom and two Cu atoms (Cu–Cu–Gd), which are bridged by one pyrimidine ring and two nitronyl nitroxides. The distance of Cu1---Cu2 is 6.197 Å, and the Cu2---Gd1 distance is 8.637 Å. The crystal packing of complex 1 is shown in Figure S3 in the SI, and the closest interlayer metal–metal distance is 10.098 Å for Cu3---Gd1#2 (#2:  $-x, -y, -z$ ).

The magnetic susceptibilities of 1 and 2 were measured in the 2–300 K temperature range under 1 kOe (Figure 3). For

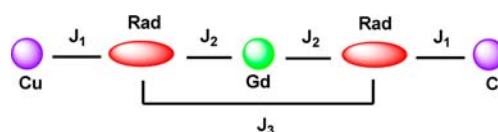


**Figure 3.**  $\chi_M T$  versus *T* plots for 1 (rhombus) and 2 (circle). The solid line represents the calculated behavior for 1.

complex 1, the  $\chi_M T$  value at 300 K is  $10.94 \text{ cm}^3 \text{ K mol}^{-1}$ , which is slightly higher than the theoretical value of  $9.76 \text{ cm}^3 \text{ K mol}^{-1}$  for the uncoupled spins of one  $\text{Gd}^{\text{III}}$  ( $S_{\text{Gd}} = 7/2$ ), two radicals ( $S_{\text{rad}} = 1/2$ ), and three  $\text{Cu}^{\text{II}}$  ( $S_{\text{Cu}} = 1/2$ ), assuming  $g = 2.0$ . Upon lowering of the temperature, the  $\chi_M T$  value increases more and more rapidly to reach  $18.81 \text{ cm}^3 \text{ K mol}^{-1}$  at 2.0 K. Such a behavior is characteristic of a system with ferromagnetic interactions. The molar susceptibility obeys the Curie–Weiss law with the Curie constant of  $C = 10.90 \text{ cm}^3 \text{ K mol}^{-1}$  and a positive Weiss constant of  $\theta = 5.01 \text{ K}$ . On the basis of the crystal structure, five main

magnetic exchange interactions should be operative, namely, (i)  $\text{Cu}^{\text{II}}$ —directly coordinated nitroxide group ( $J_1$ ), (ii)  $\text{Gd}^{\text{III}}$ —directly coordinated NO group ( $J_2$ ), (iii) two coordinated NO groups through the  $\text{Gd}^{\text{III}}$  ion ( $J_3$ ), (iv)  $\text{Cu}^{\text{II}}$ — $\text{Cu}^{\text{II}}$  through the pyrimidine ring ( $J_4$ ), and (v) copper(II)—nitroxide group through phenyl and pyrimidine rings ( $J_5$ ). The last magnetic interaction should be weak; however, it may be ferromagnetic according to the spin-polarization mechanism<sup>17</sup> (Chart S1 in the SI). The magnetic orbital of the  $\text{Cu}^{\text{II}}$  ion is defined by short equatorial bonds, and it is of the  $d_{x^2-y^2}$  type with a very small admixture  $d_z^2$ . Because the pyrimidine ring bridges two  $\text{Cu}^{\text{II}}$  ions through axial–axial positions and the out-of-plane exchange pathway is involved, the magnetic coupling between two  $\text{Cu}^{\text{II}}$  ions via the pyrimidine ring ( $J_4$ ) is anticipated to be weak. Hence, the magnetic behavior of 1 can be interpreted as that of one linear Cu–rad–Gd–rad–Cu magnetic unit plus an uncoupled  $\text{Cu}^{\text{II}}$  ion (Scheme 1 and Figure S2 in the SI). For this linear five-spin

### Scheme 1. Magnetic Exchange Coupling Unit



system, the magnetic susceptibility data cannot be analyzed by using a Kambe vector-coupling method. Thus, the magnetism package *MAGPACK*<sup>18</sup> based on the Hamiltonian  $\hat{H} = -2J_1(\hat{S}_{\text{Rad1}}\hat{S}_{\text{Cu1}} + \hat{S}_{\text{Rad2}}\hat{S}_{\text{Cu2}})$  has been em-

$$- 2J_2(\hat{S}_{\text{Rad1}}\hat{S}_{\text{Gd}} + \hat{S}_{\text{Rad2}}\hat{S}_{\text{Gd}}) - 2J_3\hat{S}_{\text{Rad1}}\hat{S}_{\text{Rad2}}$$

ployed to simulate the susceptibility data, and a good agreement between the observed and calculated values of the magnetic susceptibility is obtained, yielding the parameters  $g = 2.10$ ,  $J_1 = 20.50 \text{ cm}^{-1}$ ,  $J_2 = 3.35 \text{ cm}^{-1}$ , and  $J_3 = -6.95 \text{ cm}^{-1}$ . These results indicate that the Gd–Rad interaction is ferromagnetic, whereas the magnetic interaction between the radicals through the Gd atom is antiferromagnetic, as was already observed in other gadolinium nitronyl nitroxide compounds.<sup>9a,19</sup> The axial  $\text{Cu}^{\text{II}}$ –ON bond will result in orbital orthogonality of the  $\text{Cu}^{\text{II}}$  magnetic orbital ( $d_{x^2-y^2}$ ) and the radical  $\pi^*$  magnetic orbital; thus, the magnetic interaction between the  $\text{Cu}^{\text{II}}$  ion and the directly coordinated NO group should be ferromagnetic, and the obtained magnetic exchange coupling ( $J_1 = 20.50 \text{ cm}^{-1}$ ) is comparable with those found for similar copper(II) nitronyl nitroxide complexes.<sup>15,20</sup> A magnetization of  $12.39 \text{ N}\beta$  is reached at 7 T, corresponding to the expected saturation value of  $12 \text{ N}\beta$ . The experimental magnetization value is higher than the magnetization predicted by the Brillouin function for non-coupled one  $S = 7/2$  and five  $S = 1/2$  spins ( $g = 2.0$  and  $T = 2 \text{ K}$ ), supporting the ferromagnetic interactions in this compound. Moreover, the fitting of the isothermal magnetization *M* versus *H* curve using the same parameter as that for  $\chi_M T$  gave quite good agreement (Figure 3), which supported the  $\chi_M T$  simulation above. Furthermore, alternating-current (ac) magnetic susceptibility measurements indicate that there is no magnetic ordering above 2 K for 1 (Figure S7 in the SI).

For complex 2, the  $\chi_M T$  value at room temperature is  $17.06 \text{ cm}^3 \text{ K mol}^{-1}$ , which is also slightly larger than the expected  $16.05 \text{ cm}^3 \text{ K mol}^{-1}$  for one uncorrelated  $\text{Dy}^{\text{III}}$  ion ( ${}^6H_{15/2}$ ), two uncorrelated radical ( $S = 1/2$ ) spins, and three uncorrelated  $\text{Cu}^{\text{II}}$  ( $S = 1/2$ ) ions. Upon cooling, the  $\chi_M T$  value gradually increases and reaches a maximum of  $18.86 \text{ cm}^3 \text{ K mol}^{-1}$  at 8.5 K and then

rapidly decreases, which indicates that the ferromagnetic interactions dominate in this compound. The reciprocal susceptibility varied as the temperature follows the Curie–Weiss law with a positive Weiss constant  $\theta = 1.89$  K and Curie constant  $C = 17.02 \text{ cm}^3 \text{ K mol}^{-1}$ . The field-dependent magnetization was recorded at 2 K (Figure S8 in the SI). The  $M$  value exhibits a fast increase of magnetization for the low field, implying the presence of ferromagnetic couplings. At high field,  $M$  increases to reach  $11N\beta$  at 70 kOe without clear saturation, suggesting the presence of a significant magnetic anisotropy and possible low-lying excited states in the compound. The temperature dependence of the ac magnetic susceptibility for **2** at different frequencies has been investigated in zero field with an ac field of 3 Oe; no frequency-dependent real ( $\chi'$ ) and imaginary ( $\chi''$ ) signals have been observed (Figure S9 in the SI). This may result from quantum tunneling of the magnetization. The application of a 2 kOe direct-current (dc) field did not change the ac signal profile (Figure S10 in the SI), indicating that the tunneling effects in zero field can be neglected for complex **2**.

In summary, we have successfully obtained the first 2D 2p–3d–4f compounds. The most intriguing finding is that the 3d and 4f metal ions can be assembled in the same molecular entity by using a nitronyl nitroxide radical with nonchelating N donor atoms. This may open up new opportunities to develop novel nitronyl nitroxide based molecular magnetic materials.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

X-ray crystallographic data in CIF format, complete experimental, crystal data and structural refinements, table of bond lengths and angles, construction of a 2D crystal structure, packing diagram, spin polarization mechanism for the magnetic interaction, and ac magnetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### ■ Corresponding Author

\*E-mail: [llicun@nankai.edu.cn](mailto:llicun@nankai.edu.cn).

### ■ Notes

The authors declare no competing financial interest.

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