doi:10.1246/cl.2012.82

Triply Radical-coordinated Gadolinium(III) Complex as a High-spin $S = 5$ Assembly

Naoya Ikegaya, Takuya Kanetomo, Rina Murakami, and Takayuki Ishida*
Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585

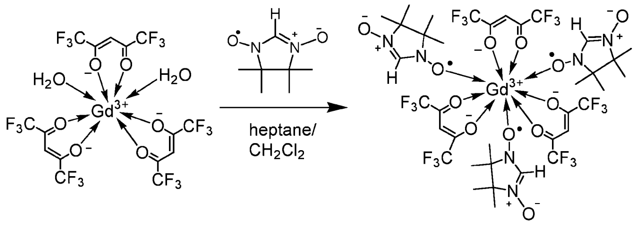
(Received October 13, 2011; CL-111006; E-mail: ishi@pc.uec.ac.jp)

A discrete Gd^{3+} and radical complex was prepared and characterized to be $[Gd(hfac)_3(HNN)_3]$ by means of X-ray crystallographic analysis, where Hhfac stands for 1,1,1,5,5,5-hexafluoropentane-2,4-dione and HNN for 4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide. A magnetic study revealed the presence of ferromagnetic exchange coupling with $2J/k_B = 3.86(6)$ K, ascribable to the Gd–HNN interaction.

Molecule-based magnetic materials have an advantage in designing a spatial arrangement of a variety of magnetic orbitals and preparing low-dimensional frameworks by means of facile self-assembly techniques.[1,2] 4f-Ion-based heterospin compounds have been intensively studied for development of bulk magnets[3] and single-molecule magnets,[4,5] where strong magnetic anisotropy and large spin are available from lanthanide (Ln) ions.[6] We have developed several single-molecule magnets and established a standard method[5,7–9] to evaluate the exchange coupling by means of high-frequency electron paramagnetic resonance.[10] In the present work, we apply a relatively small radical 4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide[11] (**HNN**) to construct novel 4f–π heterospin systems. Fortunately, in the Gd^{3+} case, the magnetic exchange coupling can be examined from the conventional $\chi(T)$ measurements, because of the spin-only character.

We newly synthesized $[Gd^{III}(hfac)_3(\mathbf{HNN})_3]$ (**Gd-HNN**), where Hhfac stands for 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Scheme 1). After a heptane solution (45 mL) of $[Gd(hfac)_3(H_2O)_2]$ (81 mg, 0.10 mmol) was heated and concentrated to a volume of ca. 15 mL, a dichloromethane solution (4 mL) of **HNN** (94 mg, 0.60 mmol) was added to the above solution while hot. The mixture was allowed to stand at room temperature and then in a refrigerator for 3 days, to give **Gd-HNN** (83 mg, 0.066 mmol) as a polycrystalline product in 66% yield. The product is stable up to the melting point (85–87 °C). To our knowledge, **Gd-HNN** is the first Ln complex with the Ln/radical ratio of 1/3, as characterized by means of X-ray crystallographic analysis[12] together with spectroscopic and elemental analyses.[13]

The Gd ion is nine-coordinate (Figure 1), where the 4f and 2p spin centers are directly bonded. The geometry of **HNN** is quite normal in comparison with some **HNN**-ligated transition-metal ion complexes.[14] A whole molecule is crystallographically independent, but the geometries around the **HNN** coordinations are similar to each other. The $Gd–O_{HNN}$ bond lengths are 2.457(2), 2.412(3), and 2.421(2) Å for Gd1–O2, Gd1–O4, and Gd1–O6, respectively. They are longer than any other related Gd complexes with aromatic **NN** ligands (typically 2.32–2.36 Å),[15] probably owing to the steric congestion of the Gd coordination sphere in **Gd-HNN**. The Gd–O–N bond angles are 134.11(17), 135.68(15), and 133.54(15)° for Gd1–O2–N2, Gd1–O4–N4, and Gd1–O6–N6, respectively. The out-of-plane Gd position from the radical conjugation plane was evaluated by the $Gd–O–N–C_\alpha$ torsion angle. The Gd1–O2–N2–C1, Gd1–O4–N4–C8, and Gd1–O6–N6–C15 angles are 37.5(4), −44.9(4), and 45.5(4)°, respectively.



Scheme 1. Synthetic route to **Gd-HNN**.

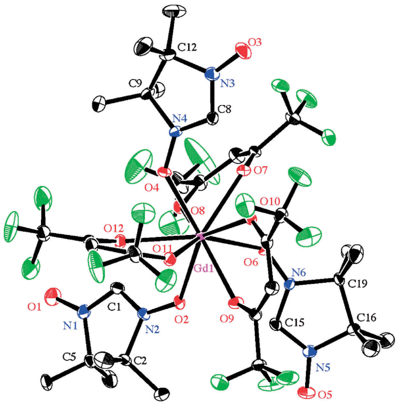


Figure 1. X-ray crystal structure of **Gd-HNN** with thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity. Selected atomic numbering is shown. Green and black atoms stand for F and C, respectively.

Magnetic susceptibility of a randomly oriented polycrystalline specimen of **Gd-HNN** was measured at 500 Oe, as a function of temperature (Figure 2). The $\chi_m T$ value at 300 K was 9.3 $cm^3 K mol^{-1}$, which is very close to the high-temperature limit of the spin-only value (9.0 $cm^3 K mol^{-1}$). The $\chi_m T$ value was increased on cooling, indicating the presence of ferromagnetic coupling. The maximum around 4.5 K was considerably smaller than the ferromagnetic limit with $S_{total} = 5$ (15 $cm^3 K mol^{-1}$). This finding suggests the presence of intermolecular antiferromagnetic coupling.[16]

The inset shows the magnetization curve of polycrystalline **Gd-HNN** measured at 4.5 K. The magnetization reached 9.16 $N_A\mu_B$ at 7 T, and the saturation magnetization is estimated to be 10 $N_A\mu_B$, being consistent with ferromagnetically correlated $S = 7/2$ and three $S = 1/2$ species with $g = 2$. The experimental data are located above the calculated curve of a noninteracting model (the broken line), but considerably smaller than that of the ferromagnetic $S_{total} = 5$ limit (the solid line). The presence of intermolecular antiferromagnetic coupling is confirmed.

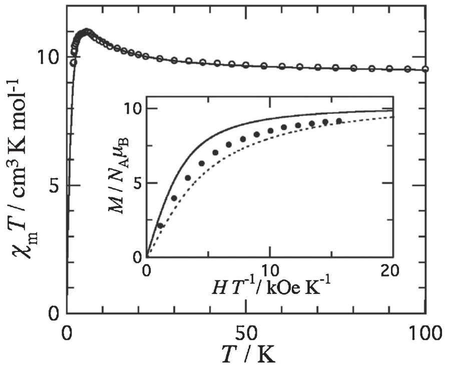


Figure 2. Temperature dependence of $\chi_m T$ for randomly oriented polycrystalline **Gd-HNN** measured at 500 Oe. A solid line shows the theoretical fit. For the equations and parameters, see the text. Inset: magnetization curve measured at 4.5 K. Solid and broken lines stand for the calculated curves with the Brillouin function (B_J) of $S = 5$ and the sum of a B_J of $S = 7/2$ and three B_J's of $S = 1/2$, respectively.

As the crystal structure analysis suggests, the molecule is assumed to have approximately threefold symmetry in the magnetic analysis. The Heisenberg spin Hamiltonian is drawn as $H = -2JS_1 \cdot (S_2 + S_3 + S_4)$, where S_1 implies the Gd^{3+} spin and $S_2 - S_4$ the **HNN** spins. The following van Vleck equation is obtained by means of Kambe's vector coupling method[17] (eq 1). A Weiss mean field parameter θ is introduced. The parameters were optimized, giving $2J/k_B = +3.86(6)$ K, $\theta = -1.052(9)$ K, and $g_{avg} = 2.0411(14)$. The calculation well reproduced the experimental data (the solid line in Figure 2). We conclude that **Gd-HNN** possesses the ground $S_{total} = 5$ state.

$$\chi_m = \frac{2N_A\mu_B{}^2 g_{avg}{}^2}{k_B(T-\theta)} \frac{A}{B} \tag{1}$$

$$\begin{aligned} A = {} & 55 + 60\exp(-7J/k_BT) + 30\exp(-10J/k_BT) \\ & + 28\exp(-15J/k_BT) + 14\exp(-18J/k_BT) \\ & + 5\exp(-24J/k_BT) \end{aligned}$$

$$\begin{aligned} B = {} & 11 + 18\exp(-7J/k_BT) + 9\exp(-10J/k_BT) \\ & + 14\exp(-15J/k_BT) + 7\exp(-18J/k_BT) \\ & + 5\exp(-24J/k_BT) \end{aligned}$$

There have been several reports on ferromagnetic coupling between Gd^{3+} and organic radicals.[15,18] Gatteschi et al. have analyzed the Gd^{3+}–PhNN interaction based on the balance of ferro- and antiferromagnetic contributions from each 4f–π^* interaction (PhNN stands for 2-phenyl-NN).[18] Similarly, in **Gd-HNN**, when the π^* orbital in **HNN** is antiferromagnetically correlated with 4f$_{z3}$ and 4f$_{xyz}$ for instance, the other combinations can be all orthogonal to the π^* orbital, possibly leading to an overall ferromagnetic coupling. Ferromagnetic Gd^{3+}–Cu^{2+} systems are also well known, and a plausible mechanism involving 5d–3d interaction and not 4f–3d overlap has been proposed.[19] An overlap of 5d–π^* might be taken into consideration for **Gd-HNN**, if it seems less likely that three nitroxide π^* orbitals are all coincidently orthogonal to 4f orbitals on Gd^{3+} with such large geometric torsion.

The nitronyl nitroxide group can bridge metal ions giving 1/1 metal–radical alternating chains, which has been applied to the first 4f–π single-chain magnets.[20] On the other hand, bulk magnetic solids require higher networking, and accordingly constructing a triply or more multiply radical-coordination seems to be a promising way.[21] Organic radicals possess sterically bulky groups for stabilization, which disturb such multicoordination. There have been several examples of 1/1 and 1/2 Ln–radical compounds.[15,18,22] The present study successfully showed a unique 1/3 ratio in **Gd-HNN**, thanks to the small size of **HNN**.

This work was partly supported by Grants-in-Aid for Scientific Research from MEXT (Nos. 22350059 and 23110711).

References and Notes

1 O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.

2 *Magnetism: Molecules to Materials I–V*, ed. by J. S. Miller, M. Drillon, Wiley-VCH, Weinheim, Germany, **1999–2005**. DOI Nos.: I, doi:10.1002/3527600841; II, doi:10.1002/3527600590; III, doi:10.1002/3527600140; IV, doi:10.1002/3527600698; V, doi:10.1002/3527604383.

3 J. Fidler, T. Schrefl, S. Hoefinger, M. Hajduga, *J. Phys.: Condens. Matter* **2004**, *16*, S455.

4 S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski, *J. Am. Chem. Soc.* **2004**, *126*, 420; F. Pointillart, K. Bernot, R. Sessoli, D. Gatteschi, *Chem.—Eur. J.* **2007**, *13*, 1602.

5 F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi, H. Nojiri, *J. Am. Chem. Soc.* **2006**, *128*, 1440.

6 N. Ishikawa, M. Sugita, T. Ishikawa, S.-y. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694.

7 S. Ueki, T. Ishida, T. Nogami, K.-Y. Choi, H. Nojiri, *Chem. Phys. Lett.* **2007**, *440*, 263.

8 A. Okazawa, T. Nogami, H. Nojiri, T. Ishida, *Chem. Mater.* **2008**, *20*, 3110; A. Okazawa, R. Watanabe, H. Nojiri, T. Nogami, T. Ishida, *Polyhedron* **2009**, *28*, 1808; A. Okazawa, K. Fujiwara, R. Watanabe, N. Kojima, S. Yoshii, H. Nojiri, T. Ishida, *Polyhedron* **2011**, *30*, 3121.

9 A. Okazawa, T. Nogami, H. Nojiri, T. Ishida, *Inorg. Chem.* **2008**, *47*, 9763; A. Okazawa, T. Nogami, H. Nojiri, T. Ishida, *Inorg. Chem.* **2009**, *48*, 3292; R. Watanabe, K. Fujiwara, A. Okazawa, G. Tanaka, S. Yoshii, H. Nojiri, T. Ishida, *Chem. Commun.* **2011**, *47*, 2110; T. Shimada, A. Okazawa, N. Kojima, S. Yoshii, H. Nojiri, T. Ishida, *Inorg. Chem.* **2011**, *50*, 10555.

10 H. Nojiri, K.-Y. Choi, N. Kitamura, *J. Magn. Magn. Mater.* **2007**, *310*, 1468; H. Nojiri, Y. Ajiro, T. Asano, J.-P. Boucher, *New J. Phys.* **2006**, *8*, 218.

11 D. G. B. Boocock, R. Darcy, E. F. Ullman, *J. Am. Chem. Soc.* **1968**, *90*, 5945.

12 Selected crystallographic data: $C_{36}H_{42}F_{18}GdN_6O_{12}$, triclinic, $P\bar{1}$, $a = 12.1493(17)$, $b = 13.803(2)$, $c = 14.861(3)$ Å, $\alpha = 84.616(8)$, $\beta = 84.077(8)$, $\gamma = 82.673(8)°$, $V = 2450.5(7)$ Å^3, μ(Mo Kα) = 1.487 mm^{-1}, $d_{calcd} = 1.694$ g cm^{-3}, $R(F)$ ($I > 2\sigma(I)$) = 0.0326; $R_W(F^2)$ (all data) = 0.0548, $T = 100$ K for unique 11126 diffractions. CCDC 846924.

13 IR (neat, attenuated total reflection): 1657, 1456, 1248, 1193, 1137, 1098, 793, 660 cm^{-1}. Anal. Calcd for $C_{36}H_{42}F_{18}GdN_6O_{12}$: C, 34.59; H, 3.39; N, 6.72%. Found: C, 34.87; H, 3.48; N, 6.89%.

14 T. Ise, T. Ishida, T. Nogami, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2463; T. Ise, T. Ishida, D. Hashizume, F. Iwasaki, T. Nogami, *Inorg. Chem.* **2003**, *42*, 6106; N. Ishii, T. Ishida, T. Nogami, *Inorg. Chem.* **2006**, *45*, 3837.

15 N. Zhou, Y. Ma, C. Wang, G.-F. Xu, J. Tang, S.-P. Yan, D.-Z. Liao, *J. Solid State Chem.* **2010**, *183*, 927, and references cited therein.

16 Intermolecular shortest distances are found at O1–C11^{i} with 3.312(5) Å, at O3–C13^{ii} with 3.376(4) Å, and at O5–C7^{iii} with 3.317(5) Å [the symmetry operation codes for i, ii, and iii are $(-x + 1, -y + 2, -z)$, $(-x + 1, -y + 2, -z + 1)$, and $(-x, -y + 1, -z)$, respectively].

17 K. Kambe, *J. Phys. Soc. Jpn.* **1950**, *5*, 48.

18 C. Benelli, A. Caneschi, D. Galleschi, J. Laugier, P. Rey, *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913; C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, *Inorg. Chem.* **1992**, *31*, 741.

19 M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J. C. Trombe, *J. Am. Chem. Soc.* **1993**, *115*, 1822.

20 L. Bogani, C. Sangregorio, R. Sessoli, D. Gatteschi, *Angew. Chem., Int. Ed.* **2005**, *44*, 5817; K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi, R. Sessoli, *J. Am. Chem. Soc.* **2006**, *128*, 7947.

21 D. Luneau, P. Rey, *Coord. Chem. Rev.* **2005**, *249*, 2591.

22 For compounds with a Ln/radical ratio of 1/4, see: C. Lescop, E. Belorizky, D. Luneau, P. Rey, *Inorg. Chem.* **2002**, *41*, 3375.