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Strongest Exchange Coupling in Gadolinium(III) and Nitroxide Coordination Compounds

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Supporting Information

ABSTRACT: The largest antiferromagnetic coupling parameter was characterized to be $2J/k_B = -15.9(2)$ K in [Gd(hfac)$_3$(6bpyNO)], where 6bpyNO stands for 2,2′-bipyridin-6-yl *tert*-butyl nitroxide. This molecule was designed according to the empirical relation: more planar chelate favors stronger antiferromagnetic coupling. The Gd−O$_{rad}$ bond is relatively short owing to the tridentate character.

Lanthanoid (Ln) coordination compounds attract much interest in the development of molecular refrigerants[1] as well as molecular magnets.[2] It is often claimed that the magnetic couplings involving Ln ions are weak, mainly because the magnetic orbitals reside in inner 4f. Stronger couplings are expected in 4f−2p heterospin systems rather than 4f−4f or 4f−3d systems. However, to improve the exchange coupling in 4f−2p systems, little is known about the magnetic coupling nature in relation with the coordination structures.[3]

A spin-only Gd^{3+} ion (4f^7, $^8S_{7/2}$) is often chosen as an initial attempt in the Ln series. Lescop et al. have pointed out that antiferromagnetic gadolinium (Gd)-radical complexes are relatively rare[4,5] among a number of reports on magnetic couplings between Gd^{3+} and organic spins.[3−8] We have proposed the empirical relation between the exchange coupling and torsion angle Gd−O−N−C(sp^2) (Figure 1),[9] although there are many geometrical parameters possibly influencing the coupling. One may find that a more planar Gd−O−N−C configuration favors stronger antiferromagnetic coupling. The critical torsion is estimated to be 36°, leaving no exception. The angular geometry would regulate ferro- or antiferromagnetic coupling, while Gd−O$_{rad}$ bonds and other geometries play an auxiliary role such as scaling. Murakami et al. extended this prescription to Tb^{3+} complexes to develop single-molecule magnets.[10] Rajaraman et al. recently reported vast density functional theory calculations on the known Gd-radical compounds and agreed with the importance of the Gd−O−N−C torsion.[11]

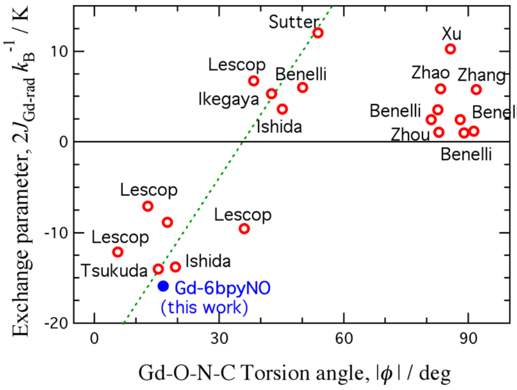
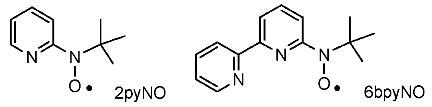


Figure 1. Plot of the exchange coupling parameter versus Gd−O−N−C(sp^2) torsion angle on the gadolinium(3+)-nitroxide complexes. Data are taken from the literature.[3−9] For normalization factors when nitroxides other than aryl *tert*-butyl nitroxides are used, see the text. A broken line implies the best fit for the data in |ϕ| < 70°.

The relatively planar chelate [Gd(hfac)$_3$(2pyNO)(H$_2$O)] (**Gd-2pyNO**) held the record [$2J_{Gd-rad}/k_B = -13.8(3)$ K][9] prior to this work, where 2pyNO stands for *tert*-butyl 2-pyridyl nitroxide (Scheme 1). To improve J_{Gd-rad}, the molecular design should be focused on the following items: (i) to flatten a chelate ring; (ii) to shorten a Gd−O$_{rad}$ bond. 2,2′-Bipyridin-6-yl *tert*-butyl nitroxide[12] (6bpyNO) is supposed to be promising for this purpose.

Scheme 1. Chelating Paramagnetic Ligands



We prepared [Gd(hfac)$_3$(6bpyNO)] (**Gd-6bpyNO**) from complexation between [Gd(hfac)$_3$(H$_2$O)$_2$][13] and 6bpyNO. A polycrystalline product as-synthesized[14] was subjected to X-ray crystallographic and magnetic studies.

The **Gd-6bpyNO** complex crystallizes in a monoclinic $P2_1/n$ space group (Figure 2).[15] The Gd^{3+} center is nine-coordinate with two N and one O atoms from the 6bpyNO chelate and six O atoms from three coligands. The *SHAPE* software[16] indicates that the coordination polyhedron can be best described as a capped square antiprism (CSAPR). The Gd1−O1, Gd1−N2, and Gd1−N3 distances are 2.373(4), 2.560(4), and 2.568(4) Å, respectively. The Gd1−O1−N1 angle is 126.2(3)°. The Gd1−O1−N1−C1 torsion angle is 16.5(5)°.

The 6bypNO ligand is tridentate, whereas 2pyNO is bidentate, leading to a different coordination structure. Actually, the nine-coordinate Gd ion in **Gd-2pyNO** has an additional aquo ligand, but its polyhedron was similarly described as CSAPR.[9] The Gd−O1−N1−C1 portion is more planar than that of **Gd-2pyNO**, as indicated with the larger torsion angle of the latter [19.5(8)°]. The tandem five-membered chelated rings (Gd1−O1−N1−

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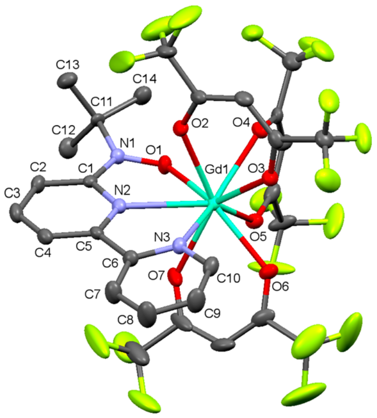

Figure 2. X-ray crystal structure of **Gd-6bpyNO** with thermal ellipsoids at the 50% level. H atoms are omitted for clarity.

C1−N2 and Gd−N2−C5−C6−N3) in **Gd-6bpyNO** seem to enhance the planar character of the Gd1−O1−N1−C1 moiety. The Gd1−O1 distance in **Gd-6bpyNO** is shorter than that of **Gd-2pyNO** [2.464(4) Å]. The tridentate ligation strengthens the bond. Thus, the molecular design described above has been realized successfully.

The magnetic susceptibility was measured for polycrystalline **Gd-6bpyNO** fixed with mineral oil in 1.8−300 K on a SQUID magnetometer (Figure 3a). The room-temperature $\chi_m T$ value of

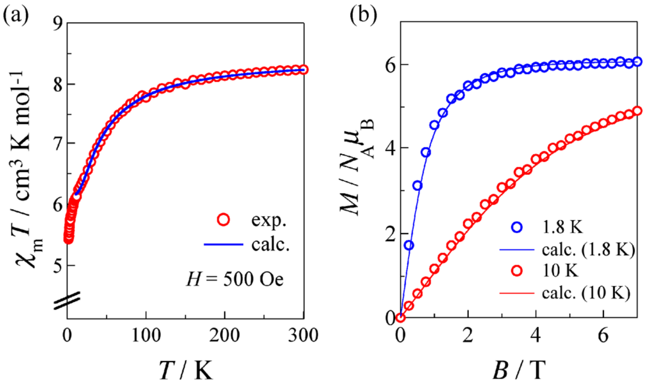

Figure 3. Temperature dependence of $\chi_m T$ at 500 Oe (a) and M versus B plots at 1.8 and 10 K (b) for **Gd-6bpyNO**. The solid lines are calculated with the Heisenberg model (a) and Brillouin function with S_{total} = 3 (b). For details, see the text.

8.24 cm^3 K mol^{-1} well agrees with the value of 8.25 cm^3 K mol^{-1} expected for a magnetically isolated Gd^{3+} ion (g = 2, S_{Gd} = $^7/_2$) and 6bpyNO (g = 2, S_{rad} = $^1/_2$). On cooling, the $\chi_m T$ value decreases around 100 K and approaches 6.06 cm^3 K mol^{-1} at 9 K, which corresponds to the ground state S_{total} = 3 (6.0 cm^3 K mol^{-1} in theory). This finding indicates the presence of considerably strong antiferromagnetic coupling to give a ferrimagnetic ground state. The $\chi_m T$ value reached 5.43 cm^3 K mol^{-1} at 1.8 K upon further cooling. A very small intermolecular antiferromagnetic interaction is suggested but disregarded for the purpose of the present study. The experimental data for **Gd-6bpyNO** at 9−300 K was analyzed with an expression (eq 1) derived from a Heisenberg spin Hamiltonian, $\hat{H} = -2J_{Gd-rad}\hat{S}_{Gd}\cdot\hat{S}_{rad}$.

$$\chi_m T = \frac{4N_A g^2 \mu_B{}^2}{k_B} \frac{7 + 15\exp(-8J_{Gd\text{-}rad}/k_B T)}{7 + 9\exp(-8J_{Gd\text{-}rad}/k_B T)} \tag{1}$$

The best fit was obtained with $2J_{Gd\text{-}rad}/k_B = -15.9(2)$ K and g = 2.024(1) (a solid line in Figure 3a). This exchange is the strongest in the Gd-nitroxide compounds ever reported.[3−9]

The field dependence of magnetization of **Gd-6bpyNO** at 1.8 and 10 K is shown in Figure 3b. The calculated curves from the Brillouin function with S_{total} = 3 and g = 2 (solid lines) almost reproduce the experimental data (open circles). We confirmed the antiferromagnetic coupling between Gd^{3+} and 6bpyNO.

The present data point has been superposed to Figure 1, which approximately obeys the empirical relation. The outline should be explained here, although details have already been described elsewhere.[9] Some Gd-radical chelates exhibit antiferromagnetic couplings, but in contrast Gd-radical compounds without chelation mostly show ferromagnetic couplings.[3−9] The Gd−O−N−C(sp^2) torsion angle ϕ is convenient, and antiferromagnetic coupling is observed only when ϕ is small. The $J_{Gd\text{-}rad}$ values of the nitronyl[17] and imino nitroxide[18] derivatives were normalized by factors of 1.37 and 1.15, respectively, to participate in the same plot[9] because the magnetic exchange coupling is proportional to the spin densities at the interacting atoms.[19] The spin density was determined on related compounds by means of polarized neutron diffraction[20] and electron-spin-resonance studies.[17,18]

The antiferromagnetic coupling observed here can be understood as follows. Every 4f orbital in Gd^{3+} carries a spin. Although the 4f lobe directions are unclear at present, we reasonably expect appreciable orbital overlaps between the Gd 4f and nitroxide π^* orbitals that offer antiferromagnetic coupling. The observed magnetic interaction usually consists of the sum of the ferro- and antiferromagnetic terms. When ferromagnetic contribution is negligible, the other becomes obvious.

The organic radical has a π^* orbital perpendicular to the molecular plane. Possible charge transfer (CT) from nitroxide (π^*) to Gd^{3+} (5d) would make the ferromagnetic state stabilized,[11] when the Gd−O−N−C structure is twisted.[9] The 3d−π^* orbital overlap is well established in copper(2+) and nickel(2+) complexes:[12,21] more twisted coordination brings about more 3d−π^* orbital overlap. Taking the similarity of 3d and 5d symmetries into account, we suppose that the planar Gd-nitroxide coordination structure would forbid CT and ferromagnetic interaction.

Such a CT mechanism was originally proposed by Kahn et al.[22] for Gd^{3+}−Cu^{2+} ferromagnetic couplings.[22−24] CT occurs through Gd^{3+} (5d)−Cu^{2+} (3d) interaction. The magnetic orbital of Cu^{2+} is located on the basal plane, and CT requires coplanar GdO$_2$Cu bridges.[22−25] On the other hand, ferromagnetic Gd-nitroxide coupling needs a twisted Gd−O−N−C configuration. The orbital symmetry is responsible for this contrast; namely, Cu^{2+} has a σ spin, whereas nitroxide has a π spin.

Semiquinonates are well-known as an alternative paramagnetic chelating ligand, and Caneschi et al. reported that the gadolinium(3+) 3,5-di-*tert*-butylsemiquinonate (DTBSQ) complex exhibited antiferromagnetic coupling with the parameter of −11.4 cm^{-1}.[26] This value is just comparable to that of **Gd-6bpyNO**. The five-membered DTBSQ chelate is planar, and the present mechanism seems to hold also for the Gd-DTBSQ system.

In summary, we have demonstrated the successful application of the proposed magnetostructural relationship in Gd-nitroxide heterospin systems (Figure 1) and actually recorded the strongest exchange coupling. From Figure 1, $|2J|/k_B$ would reach a 25 K class, but normal coordination bonds are assumed here. The very large antiferromagnetic coupling in the Gd^{3+}−

N_2^{3-}−Gd^{3+} triad[27] may afford a clue to a breakthrough to explore much larger exchange couplings. Furthermore, the interaction involving the Gd^{3+} ion is essential to comprehend those of other Ln^{3+} analogues. The magnitude of the coupling can be quantitatively estimated according to the chemical trend found throughout the Ln complex series.[24,28] The present magneto-structural relation is a reliable guiding principle to predict exchange coupling in Ln-radical heterospin systems.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for **Gd-6bpyNO** in CIF format. 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.

■ REFERENCES

(1) Sessoli, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 43. Chang, L.-X.; Xiong, G.; Wang, L.; Cheng, P.; Zhao, B. *Chem. Commun.* **2013**, 1055. Hooper, T. N.; Schnach, J.; Piligkos, S.; Evangelisti, M.; Brechin, E. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 4633. Evangelisti, M.; Roubeau, O.; Palacios, E.; Camon, A.; Hooper, T. N.; Brechin, E. K.; Alonso, J. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 6606.

(2) Bogani, L.; Sangregorio, S.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5817. Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.-y.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694. Mori, F.; Nyui, T.; Ishida, T.; Nogami, T.; Choi, K.-Y.; Nojiri, H. *J. Am. Chem. Soc.* **2006**, *128*, 1440.

(3) Luneau, D.; Ray, P. *Coord. Chem. Rev.* **2005**, *249*, 2591. Lescop, C.; Bussiere, G.; Beaulac, R.; Beslisle, H.; Beloeizky, E.; Rey, P.; Reber, C.; Luneau, D. *J. Phys. Chem. Solids* **2004**, *65*, 773. Xu, J.-X.; Ma, Y.; Xu, G.-F.; Wang, C.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Li, L.-C. *Inorg. Chem. Commun.* **2008**, *11*, 1356. Zhou, N.; Ma, Y.; Wang, C.; Xu, G.-F.; Tang, J.; Yan, S.-P.; Liao, D.-Z. *J. Solid State Chem.* **2010**, *183*, 927.

(4) Lescop, C.; Luneau, D.; Belorizky, E.; Fries, P.; Guillot, M.; Ray, P. *Inorg. Chem.* **1999**, *38*, 5472. Lescop, C.; Belorizky, E.; Luneau, D.; Ray, P. *Inorg. Chem.* **2002**, *41*, 3375.

(5) Tsukuda, T.; Suzuki, T.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **2002**, 1721. Lescop, C.; Luneau, D.; Rey, P.; Bussiere, G.; Reber, C. *Inorg. Chem.* **2002**, *41*, 5566.

(6) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed.* **1987**, *26*, 913. Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P.; Shum, D. P.; Carlin, R. L. *Inorg. Chem.* **1989**, *28*, 272. Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1989**, *28*, 275. Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1990**, *29*, 4223. Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1992**, *31*, 741.

(7) Sutter, J.-P.; Kahn, M. L.; Golhen, S.; Ouahab, L.; Kahn, O. *Chem.—Eur. J.* **1998**, *4*, 571. Kahn, M. L.; Sutter, J.-P.; Golhen, S.; Guionneau, P.; Ouahab, L.; Kahn, O.; Chasseau, D. *J. Am. Chem. Soc.* **2000**, *122*, 3413.

(8) Ikegaya, N.; Kanetomo, T.; Murakami, R.; Ishida, T. *Chem. Lett.* **2012**, *41*, 82.

(9) Ishida, T.; Murakami, R.; Kanetomo, T.; Nojiri, H. *Polyhedron* **2013**, *66*, 183.

(10) Murakami, M.; Ishida, T.; Yoshii, S.; Nojiri, H. *Dalton Trans.* **2013**, *42*, 13968.

(11) Gupta, T.; Raeshkumar, T.; Rajaraman, G. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14568.

(12) Osanai, K.; Okazawa, A.; Nogami, T.; Ishida, T. *J. Am. Chem. Soc.* **2006**, *128*, 14008.

(13) Richardson, M. F.; Wagner, W. F.; Sands, D. E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1275.

(14) *N*-2,2′-Bipyridin-6-yl-*N*-*tert*-butylhydroxylamine[12] (24.7 mg, 0.101 mmol) was oxidized with Ag_2O (72.1 mg, 0.311 mmol) in dichloromethane (4 mL) at room temperature for 1 h. The resultant black solid was filtered off. After a heptane solution (45 mL) of $[Gd(hfac)_3(H_2O)_2]$[13] (79.5 mg, 0.0976 mmol) was boiled and concentrated to ca. 10 mL, the above 6bpyNO solution was added to it while hot. The mixture was allowed to stand in a refrigerator. Orange prismatic polycrystals were precipitated. The yield was 56.6 mg (0.0554 mmol, 56%). Mp: 164−166 °C (dec). Anal. Calcd for $C_{29}H_{19}N_3O_7F_{18}Gd_1$: C, 34.12; H, 1.88; N, 4.12. Found: C, 33.83; H, 1.90; N, 4.22. IR (neat, attenuated total reflection): 1651, 1488, 1249, 1189, 1132, 1095, 795, 772, 659, 582 cm^{-1}.

(15) XRD data of **Gd-6bpyNO** were collected on Rigaku Saturn70 CCD and R-axis RAPID diffractometers with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Selected crystallographic data are as follows: $C_{29}H_{19}F_{18}GdN_3O_7$, fw 1020.71, monoclinic, $P2_1/n$, a = 13.467(3) Å, b = 17.045(4) Å, c = 16.692(4) Å, β = 105.43(1)°, V = 3694(2) Å^3, Z = 4, d_{calc} = 1.835 g cm^{-3}, μ(Mo Kα) = 1.939 mm^{-1}, $R(F)$ [$I > 2\sigma(I)$] = 0.0463, $R_w(F^2)$ (all data) = 0.0482, and T = 100 K for 8458 unique reflections. See the Supporting Information.

(16) Lluncll, M.; Casanova, D.; Circra, J.; Bofill, J. M.; Alcmany, P.; Alvarez, S.; Pinsky, M.; Avnir, D. *SHAPE*, version 2.1; University of Barcelona and : Barcelona, Spain, and Hebrew University of Jerusalem: Jerusalem, Israel, 2005.

(17) Boocock, D. G. B.; Darcy, R.; Ullman, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 5945.

(18) Ullman, E. F.; Call, L.; Osiecki, J. H. *J. Org. Chem.* **1970**, *35*, 3623. Ullman, E. F.; Call, L. *J. Am. Chem. Soc.* **1970**, *92*, 7210.

(19) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(20) Zheludev, A.; Barone, V.; Bonnet, M.; Delley, B.; Grand, A.; Ressouche, E.; Rey, P.; Subra, R.; Schweizer, J. *J. Am. Chem. Soc.* **1994**, *116*, 2019. Zheludev, A.; Bonnet, M.; Delley, B.; Grand, A.; Luneau, D.; Ostrom, L.; Ressouche, E.; Rey, P.; Schweizer, J. *J. Magn. Magn. Mater.* **1995**, *145*, 293.

(21) Okazawa, A.; Nogami, T.; Ishida, T. *Chem. Mater.* **2007**, *19*, 2733. Okazawa, A.; Nagaichi, Y.; Nogami, T.; Ishida, T. *Inorg. Chem.* **2008**, *47*, 8859. Okazawa, A.; Nogami, T.; Ishida, T. *Polyhedron* **2009**, *28*, 1917.

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

(23) Ramade, I.; Kahn, O.; Jeannin, Y.; Robert, F. *Inorg. Chem.* **1997**, *36*, 930. Koner, R.; Lin, H.-H.; Wei, H.-H.; Mohanta, S. *Inorg. Chem.* **2005**, *44*, 3524. Paulovic, J.; Cimpoesu, F.; Ferbinteanu, M.; Hirao, K. *J. Am. Chem. Soc.* **2004**, *126*, 3321.

(24) Ishida, T.; Watanabe, R.; Fujiwara, K.; Okazawa, A.; Kojima, N.; Tanaka, G.; Yoshii, S.; Nojiri, H. *Dalton Trans.* **2012**, *41*, 13609.

(25) Costes, J.-P.; Dahan, F.; Dupuis, A.; Laurent, J.-P. *Inorg. Chem.* **2000**, *39*, 169. Costes, J.-P.; Dahan, F.; Dupuis, A. *Inorg. Chem.* **2000**, *39*, 5994. Ueki, S.; Kobayashi, Y.; Ishida, T.; Nogami, T. *Chem. Commun.* **2005**, 5223.

(26) Caneschi, A.; Dei, A.; Gatteschi, D.; Sorace, L.; Vostrikova, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 246. Caneschi, A.; Dei, A.; Gatteschi, D.; Poussereau, S.; Sorace, L. *Dalton Trans.* **2004**, 1048.

(27) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. *Nat. Chem.* **2011**, *3*, 538.

(28) Okazawa, A.; Fujiwara, K.; Watanabe, R.; Kojima, N.; Yoshii, S.; Nojiri, H.; Ishida, T. *Polyhedron* **2011**, *30*, 3121. Shimada, T.; Okazawa, A.; Kojima, N.; Yoshii, S.; Nojiri, H.; Ishida, T. *Inorg. Chem.* **2011**, *50*, 10555. Okazawa, A.; Shimada, T.; Kojima, N.; Yoshii, S.; Nojiri, H.; Ishida, T. *Inorg. Chem.* **2013**, *52*, 13351.