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# Magnetic relaxation in mononuclear Tb complex involving nitronyl nitroxide ligand

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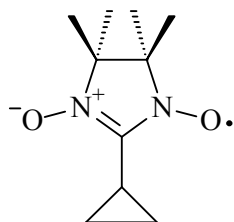
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**Abstract:** Two new lanthanide complexes with nitronyl nitroxide radicals [Ln(hfac)<sub>3</sub>(NIT-C<sub>3</sub>H<sub>5</sub>)(H<sub>2</sub>O)] (Ln<sup>III</sup> = Gd **1**, Tb **2**; NIT-C<sub>3</sub>H<sub>5</sub> = 2-cyclopropyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) have been synthesized. The two complexes possess a mononuclear structure in which the nitronyl nitroxide radical is coordinated to Ln ion as monodentate ligand through the NO group. Magnetic studies show that the lanthanide ion interacts ferromagnetically with the nitronyl nitroxide radical. Moreover, ac measurements show that Tb complex exhibits frequency-dependent out-of-phase signals suggesting single-molecule magnet behavior.

## Introduction

In the past two decades, one of the hottest trend of research in molecular magnetism is dedicated to molecule-based nanomagnets including single-molecule magnets (SMMs)<sup>1</sup> and single-chain magnets (SCMs).<sup>2</sup> The interest in such systems is justified by their possible applications in high density magnetic storage,<sup>3</sup> quantum computing,<sup>4</sup> molecular spintronics.<sup>5</sup> Among the various synthetic strategies to obtain and improve the characteristics of those molecular nanomagnets, the strategy involving lanthanide ions with radicals as ligands has proven to be very successful. For example, with

anisotropic Ln ions, a family of SCMs with different relaxation features could be obtained.<sup>6</sup> The radical-Ln based SMMs have also been reported, such as nitronyl nitroxide radical-bridged Ln dimers<sup>7</sup>, mononuclear lanthanide complexes with nitronyl nitroxide<sup>8</sup> or dithiadiazolyl radical.<sup>9</sup> Very recently, a  $N_2^{3-}$  radical bridged binuclear Tb SMM displays a record with the highest blocking temperature of 13.9K.<sup>10</sup> In spite of these reports, the radical-lanthanide based SMMs are still quite sparse. The rational design of new radical-lanthanide SMMs and the tuning of SMM properties are still great challenges. For nitronyl nitroxide-Ln complexes, several investigations have shown that the substituents of the nitronyl nitroxide radicals play the crucial role in modulating the dynamics of the magnetization.<sup>6,7c,11</sup> Along this line, we chose nitronyl nitroxide radical NIT-C<sub>3</sub>H<sub>5</sub> (NIT-C<sub>3</sub>H<sub>5</sub> = 2-cyclopropyl-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide)(Scheme 1) to construct new lanthanide-radical system. Two novel lanthanide-nitronyl nitroxide complexes, namely, [Ln(hfac)<sub>3</sub>(NIT-C<sub>3</sub>H<sub>5</sub>)(H<sub>2</sub>O)] (Ln = Gd **1**, Tb **2** and hfac = hexafluoroacetylacetonate) have been obtained. Both complexes exhibit mononuclear structure. Magnetic studies show that ferromagnetic interaction dominates in both complexes. Moreover complex **2** exhibits slow magnetic relaxation indicating single-molecule magnet behavior.



**NIT-C<sub>3</sub>H<sub>5</sub>**

Scheme 1

## Experimental Section

**Materials and Physical Measurements:** All reagents and solvents were purchased from commercial sources and used as received. The NIT-C<sub>3</sub>H<sub>5</sub> radical ligand was synthesized according to literature method.<sup>12</sup> The infrared spectra were recorded from

KBr pellets in the range 4000–400  $\text{cm}^{-1}$  with a Bruker Tensor 27 IR spectrometer. Elemental analyses for C, H, and N were carried out with a Perkin–Elmer 240 elemental analyzer. The magnetic measurements were performed with an MPMS XL-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

**Synthesis of [Gd(hfac)<sub>3</sub>(NIT-C<sub>3</sub>H<sub>5</sub>)(H<sub>2</sub>O)] (1):** Gd(hfac)<sub>3</sub>·2H<sub>2</sub>O (0.0814g, 0.1 mmol) was added in 30 mL n-heptane and heated under reflux for 3 h. After that, the solution was cooled to 60 °C, to which NIT-C<sub>3</sub>H<sub>5</sub> (0.0197g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added and stirred for 0.5 h. Then the solution was cooled to room temperature, filtrated and the filtrate was evaporated at room temperature for several days to give suitable crystals for X-ray analysis, yield 51%. Analysis C<sub>25</sub>H<sub>22</sub>GdF<sub>18</sub>N<sub>2</sub>O<sub>9</sub>: calcd: C 30.22, H 2.23, N 2.82; found: C 30.11, H 2.13, N 2.92%. IR (KBr,  $\text{cm}^{-1}$ ): 1652(s), 1501 (s), 1260 (s), 1201 (s), 1149 (s), 804 (m), 663(m).

**Synthesis of [Tb(hfac)<sub>3</sub>(NIT-C<sub>3</sub>H<sub>5</sub>)(H<sub>2</sub>O)] (2):** Complex **2** was synthesized by using the same procedure for complex **1** but with Tb(hfac)<sub>3</sub>·2H<sub>2</sub>O instead of Gd(hfac)<sub>3</sub>·2H<sub>2</sub>O. Yield: 61%. Anal. Calc. for C<sub>25</sub>H<sub>22</sub>F<sub>18</sub>TbN<sub>2</sub>O<sub>9</sub>: C, 30.16; H, 2.23; N, 2.81. Found: C,30.14; H, 2.18; N, 2.78%. IR (KBr,  $\text{cm}^{-1}$ ): 1652(s), 1499(s), 1263(s), 1203(s), 1150(s), 803(m), 662(m)  $\text{cm}^{-1}$ .

**X-ray Crystallography:** The crystallographic data for complexes **1** and **2** were collected at 113 K on a Rigaku mercury CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods by using the program SHELXS-97<sup>13</sup> and refined by full matrix least-squares methods on  $F^2$  with the use of the SHELXL-97 program package.<sup>14</sup> Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The pertinent crystallographic data and structure refinement parameters for complexes **1** and **2** were listed in Table 1. CCDC 998207 and 998208 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

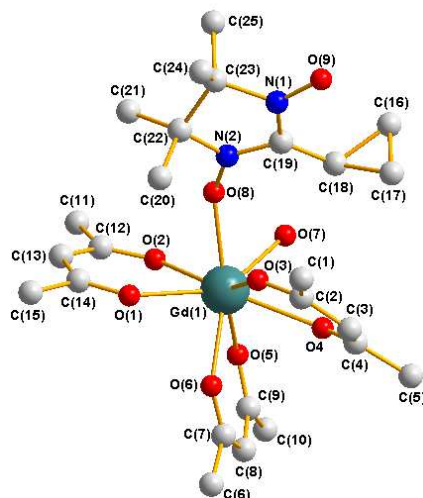
## Results and Discussion

### Synthesis

As well known, magnetic relaxation of Ln-based SMMs is very sensitive to the ligand field of lanthanide ion.<sup>15</sup> On the other hand, intramolecular magnetic coupling can suppress effectively the quantum tunneling of magnetization of rare-earth ions.<sup>10,16</sup> In order to explore the effect of the substitution of the nitronyl nitroxide on magnetic relaxation, we decided to employ cyclopropyl substituted nitronyl nitroxide to construct new nitronyl nitroxide-Ln complexes. So far, the reported nitronyl nitroxide-Ln based SMMs are based on the nitronyl nitroxide radicals with aromatic substitutions.<sup>7,8</sup> The complexes were obtained by mixing Ln(hfac)<sub>3</sub> and NIT-C<sub>3</sub>H<sub>5</sub> radical with a 1:1 ratio in heptanes at 60 °C.

### Crystal Structure

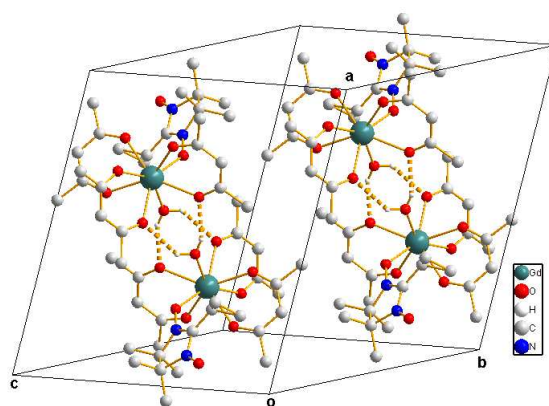
Single-crystal X-ray analysis of **1** and **2** indicates that both complexes possess isomorphous monoclear structure and crystallize in the monoclinic space group *P2<sub>1</sub>/c*. The important bond lengths and angles for **1** and **2** are listed in Table 2.



**Fig. 1.** Molecular structure of complex **1**. Hydrogen and fluorine atoms are not shown for the sake of clarity.

To each lanthanide (III) ion, there are eight coordination sites (Fig. 1, Fig. S1), which are occupied by six oxygen atoms of three hfac molecules with the Ln–O bond lengths in the range of 2.338(2)–2.491(2) for **1** and 2.315 (2)–2.466(2) Å for **2**, one oxygen atom from one NIT-C<sub>3</sub>H<sub>5</sub> radical with the Ln–O(rad) bond length of 2.318(2)

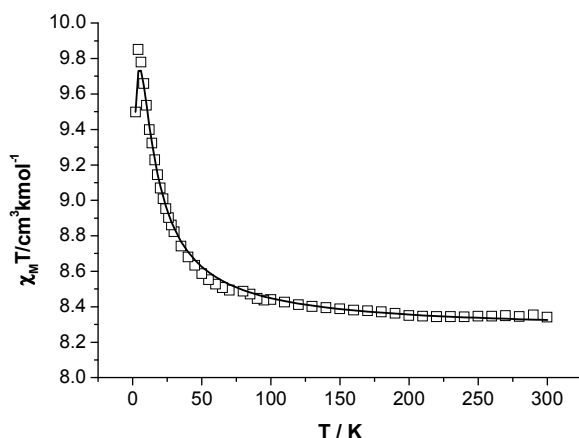
Å for **1** and 2.292(2) Å for **2**, one oxygen atom from one water molecule with the Ln–O bond length of 2.368(2) Å and 2.343(2) Å for **1** and **2**, respectively. The radical ligand is coordinated to Ln ion through the O atom of the NO group as terminal ligand. The radical ligand and the coordinated water molecule are in a *cis* configuration. The shortest Ln---Ln distance *via* space is 5.903 Å for **1** and 5.891 Å for **2**. The intermolecular hydrogen bonds, which contain O7-H7A···O5 (O···O = 2.983(3) Å with an OHO angle of 135.1°), O7-H7B···O2 (O···O = 2.751(3) Å with an OHO angle of 156.0°) for **1** and O7-H7A···O2 (O···O = 2.990(3) Å with an OHO angle of 134.7°), O7-H7B···O6 (O···O = 2.764(2) Å with an OHO angle of 153.0°) for **2**, connect two molecules into a dimer (Fig. 2 and Fig. S2).



**Fig. 2.** Crystal packing diagram of complex **1**.

### Magnetic properties

The temperature dependence of magnetic susceptibility of complexes **1** and **2** was measured in 2-300K range under 1kOe and the magnetic behaviors are shown as  $\chi_M T$  and  $\chi_M$  versus T plots in Figures 3 and 4, respectively.



**Fig. 3.** Plot of  $\chi_M T$  versus  $T$  for complex **1**. The solid line represents the best fit for **1** (see text).

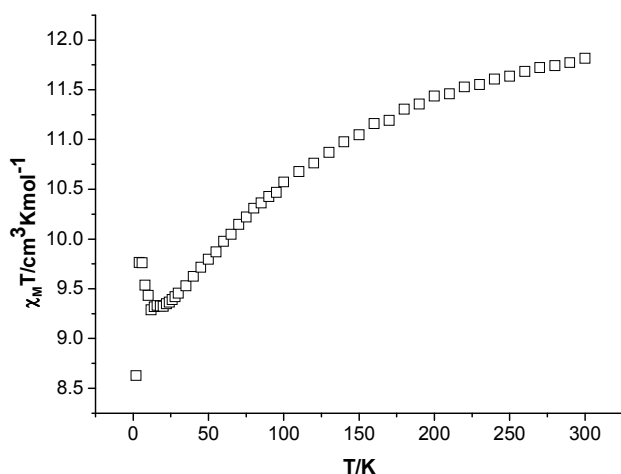
The measured  $\chi_M T$  values at 300 K are 8.34 and 11.85  $\text{cm}^3 \text{Kmol}^{-1}$  for complexes **1** and **2**, respectively. These values are close to the expected values of 8.26 and 12.20  $\text{cm}^3 \text{Kmol}^{-1}$  for **1** and **2**, respectively, for one uncoupled Ln(III) ion ( $\text{Gd}^{\text{III}} : {}^8\text{S}_{7/2}, S = 7/2, L = 0, g = 2, C = 7.88 \text{ cm}^3 \text{Kmol}^{-1}$ ;  $\text{Tb}^{\text{III}} : {}^7\text{F}_6, S = 3, L = 3, g = 3/2, C = 11.82 \text{ cm}^3 \text{Kmol}^{-1}$ ) and one organic radical ( $S = 1/2$ ). For complex **1**, upon cooling, the  $\chi_M T$  value increases more and more rapidly to reach a maximum of 9.85  $\text{cm}^3 \text{Kmol}^{-1}$  at 4.0 K, and then decreases to reach 9.50  $\text{cm}^3 \text{Kmol}^{-1}$  at 2.0 K. The magnetic behavior indicates that the ferromagnetic interaction dominates in this complex. At lower temperature, the decrease of the  $\chi_M T$  value is presumably due to antiferromagnetic intermolecular interactions. According to the crystal structure, the magnetic data were analyzed by a theoretical expression deduced from the spin Hamiltonian  $\mathbf{H} = -J\mathbf{S}_{\text{Rad}}\mathbf{S}_{\text{Gd}}$ . The possible interactions between the mononuclear complex molecules are introduced by the mean-field,  $zJ'$ .

$$\chi_{\text{RadGd}} = \frac{4Ng^2\beta^2}{kT} \frac{7 + 15 \exp(4J/kT)}{7 + 9 \exp(4J/kT)}$$

$$\chi_M = \chi_{\text{RadGd}} / [1 - (zJ' \chi_{\text{radGd}} / Ng^2\beta^2)]$$

The best fit led to  $g = 2.00$ ,  $J = 3.48 \text{ cm}^{-1}$ ,  $zJ' = -0.011 \text{ cm}^{-1}$ ,  $R = 2.72 \times 10^{-5}$  ( $R$  value is defined as  $\Sigma[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \Sigma(\chi_M)_{\text{obs}}^2$ ). The obtained  $J$  value is comparable to that

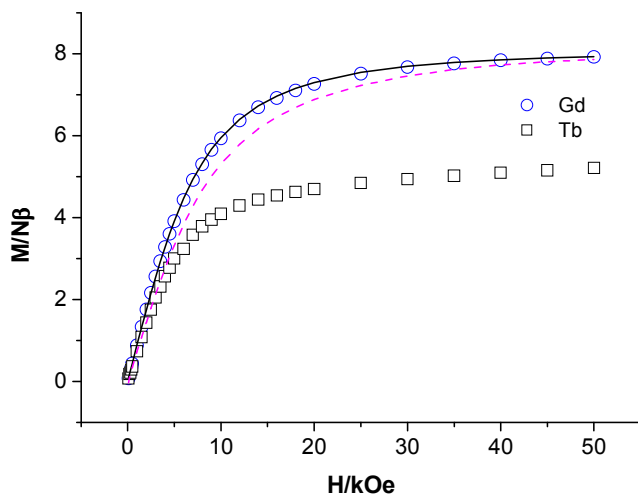
previously reported for Gd-nitronyl nitroxide compounds.<sup>17</sup> The ferromagnetic interaction between the Gd and radical can be understood as a consequence of electron transfer involving the magnetic orbital of the free radical( $\pi^*$ ) and the empty orbitals of the Gd(III) ion (5d or 6s) that stabilized the higher multiplicity ground spin state following Hund's rule.<sup>18</sup>



**Fig. 4.** Plot of  $\chi_M T$  versus T for complex **2**.

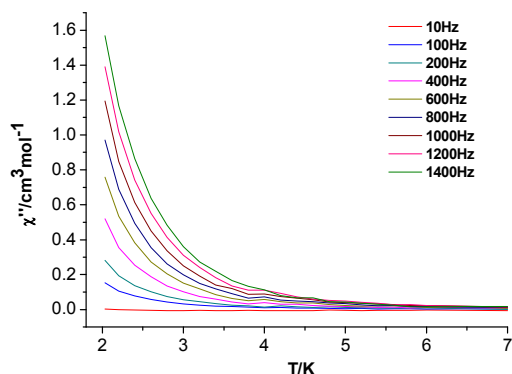
For complex **2**, on lowering the temperature,  $\chi_M T$  value gradually decreases and reaches a value of  $9.27 \text{ cm}^3 \text{Kmol}^{-1}$  at 16 K, originating from the thermal depopulation of the Tb(III) Stark sublevels, then the  $\chi_M T$  value increases to  $9.72 \text{ cm}^3 \text{Kmol}^{-1}$  at 4K, before finally decreasing abruptly. The increase of  $\chi_M T$  at low temperature suggests the presence of ferromagnetic interaction between the Tb(III) ion and the coordinated NO group of organic radical.





**Fig. 5.**  $M$  versus  $H$  plots at 2K for **1** and **2**. The solid line represents the Brillouin function for  $S = 4$  with  $g = 2.0$ , and the dotted line represents the theoretical magnetization curve for the sum of the Brillouin functions for one  $\text{Gd}^{\text{III}}$  ( $S = 7/2$ ), one radical ( $S = 1/2$ ) and  $g = 2.0$ .

The field dependence of magnetization for complexes **1** and **2** was measured at 2 K in the range of 0-50 kOe. The  $M$  versus  $H$  curves are shown in Figure 5. For complex **1**, the magnetization value at 50 kOe is  $7.92N\beta$ , corresponding to the expected saturation values of  $8.0 N\beta$ . The experimental magnetization is above the magnetization calculated with the Brillouin function for non-coupled  $S = 7/2$  and  $S = 1/2$  spin centers ( $g = 2.0$ ,  $T = 2$  K), but is well reproduced by the Brillouin function with  $S = 4$  and  $g = 2.0$ , which supports that complex **1** has an  $S = 4$  spin ground state resulting from the Gd-radical ferromagnetic interaction. For complex **2**,  $M$  versus  $H$  curve shows a rapid increase at low magnetic field, which is consistent with the presence of intramolecular ferromagnetic interaction. The magnetization eventually reaches the value of  $5.23 N\beta$  at 50 kOe, which does not achieve a complete saturation. This behavior suggests the presence of a significant magnetic anisotropy and/ or more likely the presence of low-lying excited states.<sup>19</sup>



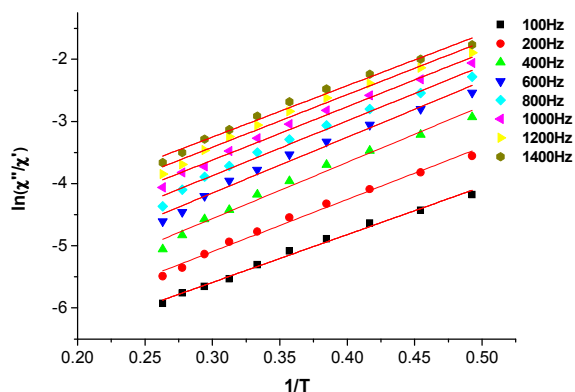
**Fig. 6.** Temperature dependence of out-of-phase components of the ac magnetic susceptibility in zero dc field with an oscillation 2.7 Oe for complex **2**.

To probe the possible SMM behavior, ac magnetic susceptibility measurements as a function of the temperature were performed on **2** at different frequencies under zero-external field. The frequency dependent out-of-phase signals are observed below 5K, but no peak maximum is found above 2 K (Figure 6). This behavior could be due to the existence of a fast quantum tunneling relaxation of the magnetization (QTM). Thus, ac measurements were performed under a small external dc field of 1000 Oe, to fully or partly suppress the possible fast quantum tunneling relaxation. The frequency dependent in-phase signals show peak maximum at high frequencies, the out-of-phase signals still do not exhibit any maximum at frequencies reaching 1400 Hz (Figure S4). We are unable to determine the energy barrier  $U_{\text{eff}}$  and  $\tau_0$  via the conventional Arrhenius plot method because no maxima in  $\chi''$  are observed. Alternative method, recently employed by Bartolomé et al., is to assume that there is only one characteristic relaxation process of the Debye type with one energy barrier and one time constant.<sup>20</sup> With this assumption, one obtains the following relation

$$\ln(\chi''/\chi') = \ln(\omega\tau_0) + U_{\text{eff}}/k_{\text{B}}T$$

From this expression, one can extract an estimate of the activation energy and the characteristic time through fitting the experimental data. The best fit yielded  $U_{\text{eff}} \approx 8.53\text{K}$  and  $\tau_0 \approx 2.26 \times 10^{-6}\text{ s}$ , and  $U_{\text{eff}} \approx 10.34\text{ K}$  and  $\tau_0 \approx 3.40 \times 10^{-6}\text{ s}$  for zero and 1kOe filed, respectively. As seen, the anisotropic energy barrier ( $U_{\text{eff}}$ ) slightly increases in an applied dc field. The obtained  $\tau_0$  value is agreement with the expected characteristic

relaxation time  $10^{-6}$ – $10^{-11}$  s for SMMs.<sup>1c,d</sup> These suggest complex **2** may be SMMs.



**Fig. 7.** Natural logarithm of the ratio of  $\chi''$  to  $\chi'$  vs.  $1/T$  for complex **2** (zero dc field). The solid line represents the fitting results.

## Conclusion

Two new mononuclear Ln-radical complexes have been prepared by using non-chelating nitronyl nitroxide radical. The magnetic interaction between the Ln ion and the radical is ferromagnetic. Slow magnetic relaxation was observed in Tb complex indicating SMM behavior. In contrast with the Dy-based SMMs, there are scarce reports on Tb-based SMMs because the bistability is not guaranteed for non-Kramer Tb(III) ion. In that regards, the Tb-nitronyl nitroxide approach is an appealing way to obtain Tb-based SMMs due to the ferromagnetic coupling between Tb ion and nitroxide radical through the coordinated NO group which should result in magnetic ground state.

## Acknowledgements

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## References

- (a) R. Sessoli, H. L. Tsai, A.R. Shake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* 1993,**115**, 1804; (b) R.

- Sessoli, D. Gatteschi, M. A. Novak, *Nature* 1993, **365**, 141;(c) D. Gatteschi, R. Sessoli, *Angew. Chem., Int. Ed.* 2003, **42**, 268;(d) D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, UK, 2006; (e) M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A. M. Talarico, M.-A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, *Nature Mater.* 2009, **8**, 194; (f) M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, R. Sessoli, *Nature* 2010, **468**, 417; (g) D. N. Woodruff, R.E.P. Winpenny, R.A. Layfield, *Chem. Rev.* 2013, **113**, 5110.
2. (a) A. Caneschi, D. Gatteschi, N. Lalioiti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M.G Pini, M.A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760; (b) R. Clerac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem.Soc.* 2002, **124**, 12837; (c) L. Bogani, A. Vindigni, R. Sessoli, D. Gatteschi, *J. Mater.Chem.* 2008, **18**, 4750; (d) C. Coulon, H. Miyasaka, R. Clérac, *Struct. Bonding* 2006, **122**, 163; (e) H.L. Sun, Z.M. Wang, S. Gao, *Coord. Chem. Rev.* 2010, **254**, 1081; (f) W.X. Zhang, R. Ishikawa, B. Breedlove, M. Yamashita, *RSC Adv.* 2013, **3**, 3772.
3. M. N. Leuenberger, D. Loss, *Nature* 2001,**410**, 789.
4. (a) F. Troiani, M. Affronte, *Chem. Soc. Rev.* 2011, **40**, 3119; (b) J. Lehmann, A. Gaita-Ariño, E. Coronado, D. Loss, *Nat. Nanotechnol.* 2007, **2**, 312; (c) M. Ganzhorn, S. Klyatskaya, M. Ruben, W. Wernsdorfer, *Nat. Nanotechnol.*, 2013, **8**, 165.
5. (a) E. Coronado, P. Day, *Chem. Rev.* 2004, **104**, 5419; (b) L. Bogani, W. Wernsdorfer, *Nat. Mater.* 2008, **7**, 179.
6. (a) L. Bogani, C. Sangregorio, R. Sessoli, D. Gatteschi, *Angew. Chem. Int. Ed.* 2005, **44**, 5817; (b) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi, R. Sessoli, *J. Am. Chem. Soc.* 2006, **128**, 7947; (c) K. Bernot, L. Bogani, R. Sessoli, D. Gatteschi, *Inorg. Chim. Acta*, 2007, **360**, 3807.
7. (a) G. Poneti, K. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer, D. Gatteschi, *Chem. Commun.* 2007, **18**, 1807; (b) J.X. Xu, Y. Ma, D.Z. Liao, G.F. Xu, J.K.Tang, C. Wang, N. Zhou, S.P. Yan, P. Cheng, L.C. Li, *Inorg. Chem.* 2009, **48**, 8890; (c) H.X. Tian, R.N. Liu, X.L. Wang, P.P.Yang, Z.X. Li, L.C. Li, D.Z. Liao, *Eur. J. Inorg. Chem.* 2009, **29**, 4498; (d) X.L. Mei, R.N. Liu, C. Wang, P. P. Yang, L. C. Li,

- D. Z. Liao, *Dalton Trans.* 2012, **41**, 2904.
8. (a) E. Coronado, C. Giménez-Saiz, A. Recuenco, A. Tarazón, F.M. Romero, A. Camón, F. Luis, *Inorg. Chem.* 2011, **50**, 7370; (b) X.L. Wang, L.C. Li, D.Z. Liao, *Inorg. Chem.* 2010, **49**, 4735;
- (c) N. Zhou, Y. Ma, C. Wang, G.F. Xu, J.K. Tang, J.X. Xu, S.P. Yan, P. Cheng, L.C. Li, D.Z. Liao, *Dalton Trans.* 2009, **40**, 8489; (d) K. Bernot, F. Pointillart, P. Rosa, M. Etienne, R. Sessoli, D. Gatteschi, *Chem. Commun.* 2010, **46**, 6458; (e) X.-L. Mei, Y. Ma, L.-C. Li, D.-Z. Liao, *Dalton Trans.*, 2012, **41**, 505.
9. E.M. Fatila, M. Rouzières, M.C. Jennings, A.J. Lough, R. Clérac, K.E. Preuss, *J. Am. Chem. Soc.* 2013, **135**, 9596.
10. J.D. Rinehart, M. Fang, W.J. Evans, J.R. Long, *J. Am. Chem. Soc.* 2011, **133**, 14236.
11. (a) R.N. Liu, Y. Ma, P.P. Yang, X.Y. Song, G.F. Xu, J.K. Tang, L.C. Li, D.Z. Liao, S.P. Yan, *Dalton Trans.* 2012, **39**, 3321; (b) R.N. Liu, C.M. Zhang, X.L. Mei, P. Hu, H. X. Tian, L.C. Li, D.Z. Liao, J.P. Sutter, *New J. Chem.* 2012, **36**, 2088.
12. Y. Hosokoshi, M. Takahashi, T. Goto, K. Inoue, *J. Mag. and Mag. Mater.* 1998, **177-181**, 713.
13. G.M. Sheldrick, SHELXS-97, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997.
14. G.M. Sheldrick, SHELXL-97, *Program for the refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
- 15.(a) F. Branzoli, P. Carretta, M. Filibian, G. Zoppellaro, M. J. Graf, J. R. Galan-Mascaros, O. Fuhr, S. Brink and M. Ruben, *J. Am. Chem. Soc.*, 2009, **131**, 4387; (b) S. Takamatsu, T. Ishikawa, S. Y. Koshihara and N. Ishikawa, *Inorg. Chem.*, 2007, **46**, 7250.
16. J. Long, F. Habib, P. H. Lin, I. Korobkov, G. Enright, L. Ungur, W. Wernsdorfer, L. F. Chibotaru, M. Murugesu, *J. Am. Chem. Soc.* 2011, **133**, 5319.
17. (a) C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, *Inorg. Chem.* 1992, **31**, 741; (b) J.P. Sutter, M.L. Kahn, S. Golhen, L. Ouahab, O. Kahn, *Chem. Eur. J.* 1998, **4**, 571.
18. (a) C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou, L. Pardi, *Inorg. Chem.* 1990,

**29**, 1750; (b) M. Andruh, I. Ramade, E. Godjovi, O. Guillou, O. Kahn, J.C. Trombe, *J. Am. Chem. Soc.* 1993, **115**, 1822.

19. P.H. Lin, W.B. Sun, M.F. Yu, G.M. Li, P.F. Yan, M. Murugesu, *Chem. Commun.* 2011, **47**, 10993.

20. (a) F. Luis, J. Bartolomé, J.F. Fernández, J. Tejada, J.M. Hernández, X.X. Zhang, R. Ziolo, *Phys. Rev. B* 1997, **55**, 11448; (b) J. Bartolomé, G. Filoti, V. Kuncser, G. Schinteie, V. Mereacre, C.E. Anson, A.K. Powell, D. Prodius, C. Turta, *Phys. Rev. B* 2009, **80**, 014430.

Table 1 Crystal data and structure refinements for complexes **1** and **2**.

Complex	<b>1</b>	<b>2</b>
Formula	C <sub>25</sub> H <sub>22</sub> F <sub>18</sub> GdN <sub>2</sub> O <sub>9</sub>	C <sub>25</sub> H <sub>22</sub> F <sub>18</sub> TbN <sub>2</sub> O <sub>9</sub>
Formula weight	993.70	995.37
Crystal system	monoclinic	monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	15.996(3)	15.978(3)
<i>b</i> (Å)	14.115(3)	14.130(3)
<i>c</i> (Å)	16.603(3)	16.588(3)
$\beta$ (°)	113.26(3)	113.08(3)
<i>V</i> (Å <sup>3</sup> )	3443.9(1)	3445.3(1)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> (g·cm <sup>-3</sup> )	1.917	1.919
<i>F</i> (000)	1936	1940
Reflns collected	28260	26485
Independent reflns	6070	6057
<i>R</i> (int)	0.0382	0.0335
GOF on <i>F</i> <sup>2</sup>	1.064	0.996
Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.0260, <i>wR</i> <sub>2</sub> =0.0620	<i>R</i> <sub>1</sub> =0.0238, <i>wR</i> <sub>2</sub> =0.0583
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.0295, <i>wR</i> <sub>2</sub> =0.0636	<i>R</i> <sub>1</sub> =0.0263, <i>wR</i> <sub>2</sub> =0.0596
Max/min(e Å <sup>-3</sup> )	0.694/-0.606	0.731/-0.606

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

complex 1			
Gd(1)-O(1)	2.338(2)	Gd(1)-O(2)	2.491(2)
Gd(1)-O(3)	2.409(2)	Gd(1)-O(4)	2.430(2)
Gd(1)-O(5)	2.381(2)	Gd(1)-O(6)	2.355(2)
Gd(1)-O(7)	2.368(2)	Gd(1)-O(8)	2.318(2)
N(2)-O(8)	1.322(3)	N(1)-O(9)	1.325(3)
O(1)- Gd(1)-O(4)	143.70(7)	O(1)- Gd(1)-O(5)	109.83(7)
O(1)- Gd(1)-O(8)	82.92(7)	O(2)- Gd(1)-O(3)	147.52(6)
O(2)- Gd(1)-O(4)	142.53(6)	O(2)- Gd(1)-O(5)	73.22(7)
O(2)- Gd(1)-O(6)	114.27(7)	O(2)- Gd(1)-O(7)	78.25(7)
O(2)- Gd(1)-O(8)	78.55(7)	O(3)- Gd(1)-O(4)	67.76(7)
O(3)- Gd(1)-O(5)	138.64(7)	O(3)- Gd(1)-O(6)	79.94(7)
O(3)- Gd(1)-O(7)	109.86(7)	N(2)-O(8)-Gd(1)	138.09(2)
complex 2			
Tb(1)-O(8)	2.292(2)	Tb(1)-O(5)	2.315 (2)
Tb(1)-O(1)	2.328 (2)	Tb(1)-O(7)	2.343(2)
Tb(1)-O(2)	2.354 (2)	Tb(1)-O(4)	2.378(2)
Tb(1)-O(3)	2.396(2)	Tb(1)-O(6)	2.466(1)
N(1)- O(8)	1.324(3)	N(2)-O(9)	1.325(3)
O(8)-Tb(1)-O(5)	83.19(6)	O(8)-Tb(1)-O(1)	145.86(6)
O(5)-Tb(1)-O(7)	142.09(6)	O(1)-Tb(1)-O(7)	140.87(6)
O(8)-Tb(1)-O(2)	140.91(6)	O(5)-Tb(1)-O(2)	109.81(6)
O(8)-Tb(1)-O(4)	74.96(6)	O(5)-Tb(1)-O(4)	87.93 (7)
O(1)-Tb(1)-O(4)	79.75(6)	O(7)-Tb(1)-O(4)	110.35(7)
O(2)-Tb(1)-O(4)	139.67(6)	O(8)-Tb(1)-O(3)	114.82(6)



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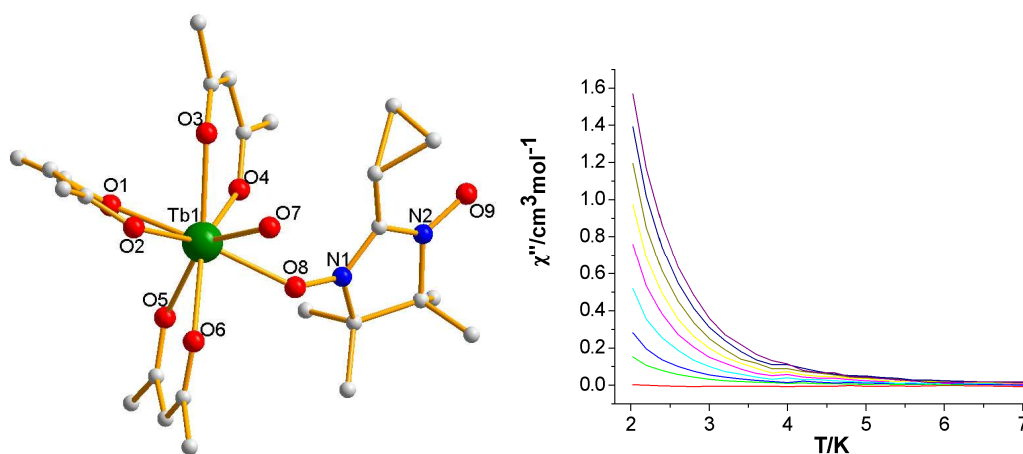
O(5)-Tb(1)-O(3)	143.36(6)	N(1)-O(8)-Tb(1)	137.09 (2)
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## Graphical Abstract

### Magnetic relaxation in mononuclear Tb complex involving nitronyl nitroxide ligand

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Novel mononuclear Tb-nitronyl nitroxide complex has been obtained, which exhibits SMM behavior.