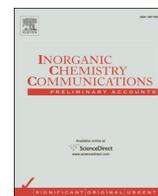




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Short communication

Structure and magnetic properties of two one-dimensional lanthanide-nitronyl nitroxide biradical compounds

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ABSTRACT

Two novel lanthanide-biradical complexes $[\text{Ln}(\text{hfac})_3(\text{BNPhOEt})] \cdot \text{C}_6\text{H}_{14}$ ($\text{Ln}^{\text{III}} = \text{Gd}$ **1**, Dy **2**; $\text{hfac} = \text{hexafluoroacetylacetonate}$; $\text{BNPhOEt} = 1,2\text{-[bis-2,2'-(4,4,5,5\text{-tetramethylimidazolyl-1-oxyl-3-oxide)phenoxy]ethane}$) have been isolated and magnetically characterized. Both complexes consist of neutral one-dimensional chain in which the BNPhOEt biradical bridges two $\text{Ln}(\text{hfac})_3$ units through the NO groups. Magnetic investigations show that the $\text{Gd}(\text{III})$ ion interacts ferromagnetically with the directly NO group while the antiferromagnetic interaction was observed between two NO groups through the $\text{Gd}(\text{III})$ ion. Moreover, complex Dy exhibits the field induced magnetic relaxation behavior.

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The use of stable organic radicals as building blocks is a promising strategy towards constructing molecular nanomagnets [1–3]. Various species ranging from mono- and binuclear SMMs [4,5] to SCMs with various relaxation features [6] have been obtained by using this strategy, particularly a binuclear Tb compound bridged by N_2^{3-} radical displays the high blocking temperature of 13.9 K [7]. However, most of reported radical-based molecular nanomagnets are constructed from monoradicals [4–8]. In contrast, very few biradical-based nanomagnets have been obtained [9] and the use of organic biradicals is relatively less explored. Nitronyl nitroxide biradical is a very appealing radical ligand owing to its four NO groups which may perform coordination function to bind metal ions generating interesting topologies [10]. In this regard, Gatteschi et al. have reported one mononuclear Dy -biradical complex exhibiting SMM behavior [11]. Very recently Vaz et al. have successfully synthesized a family of Ln -radical compounds involving bis(imino nitroxide) biradical and dinuclear complex $[\text{Dy}_2(\text{hfac})_6(\text{IPhIN})(\text{H}_2\text{O})_2]$ displays a field induced slow relaxation of magnetization behavior [12]. In order to further explore novel biradical-metal system, we employ nitronyl nitroxide biradical BNPhOEt ($\text{BNPhOEt} = 1,2\text{-[bis-2,2'-(4,4,5,5\text{-tetramethylimidazolyl-1-oxyl-3-oxide)phenoxy]ethane}$) (Scheme 1) to react with lanthanides for building new Ln -biradical compounds. Two new lanthanide-biradical complexes, namely, $[\text{Ln}(\text{hfac})_3(\text{BNPhOEt})] \cdot \text{C}_6\text{H}_{14}$ ($\text{Ln}^{\text{III}} = \text{Gd}$ **1**, Dy **2**) have been achieved.

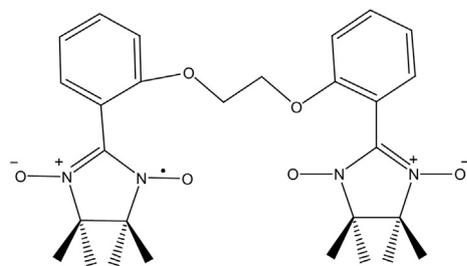
Both compounds reveal one-dimensional chain structure. Furthermore, Dy complex exhibits slow relaxation of magnetization.

Reaction of BNPhOEt biradical with $\text{Ln}(\text{hfac})_3$ ($\text{Ln}^{\text{III}} = \text{Gd}$, Dy) in hexane affords red crystals of **1** and **2**, respectively. Crystal data collection and refinement parameters are summarized in Table S1. The important bond lengths and angles are listed in Table 1.

Single-crystal X-ray diffraction analyses reveal that complexes **1** and **2** are isostructural. The asymmetric unit includes one $\text{Ln}(\text{hfac})_3$ unit, one BNPhOEt biradical ligand and one hexane solvent molecule. As shown in Fig. 1 and S1, every BNPhOEt biradical bridges two $\text{Ln}(\text{hfac})_3$ units through two NO groups from two mono-radicals to form one-dimensional chain structure. Each $\text{Ln}(\text{III})$ ion is eight-coordinated with six oxygen atoms from three hfac ligands and two oxygen atoms from two NO groups. The analysis of SHAPE software [13,14] shows that the $\text{Ln}(\text{III})$ ion is located in a distorted dodecahedron with triangular faces (D_{2d} , Table 2).

The $\text{Ln-O}(\text{radical})$ bond lengths are 2.339(7) and 2.310(9) Å for **1** and **2**, respectively, similar to other lanthanide-nitronyl nitroxide radical complexes [15–17]. The $\text{O}_{\text{Rad}}\text{-Ln-O}_{\text{Rad}}$ angles are 137.6(3)° for **1** and 136.9(4)° for **2**. The Ln-O-N-C torsion angles in complexes **1** and **2** are 90.31(1)° and 89.89(2)°, respectively. The dihedral angles between ON-C-NO group and phenyl ring for two mono-radicals are 50.72(5)° and 50.92(5)° for **1** and 52.27(6)° and 52.23(6)° for **2**. The nearest intrachain $\text{Ln}\cdots\text{Ln}$ distances are 11.149 and 11.135 Å for compounds **1** and **2**, respectively. The packing diagrams of the both complexes are shown in Fig. 2 and S2. The shortest interchain $\text{Ln}\cdots\text{Ln}$ separation in complexes **1** and **2** are 10.984 and 10.932 Å, respectively.

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Scheme 1. BNPhOEt biradical ligand.

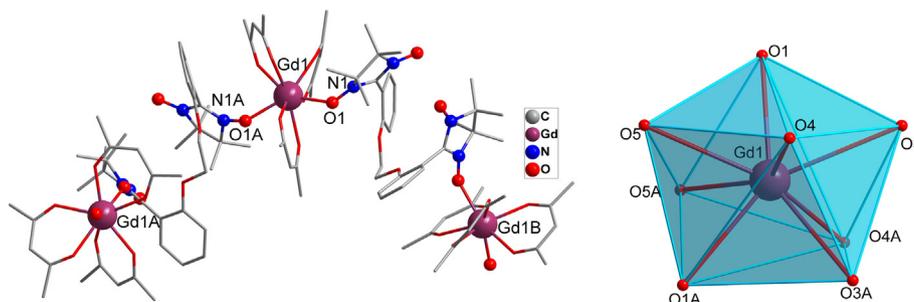
Table 1
The important bond lengths [Å] and angles [°] for complexes **1** and **2**.

Complex	1	2
Ln–O(rad)	2.339(7)	2.310(9)
Ln–O(hfac)	2.350(7)–2.411(8)	2.319(9)–2.364(10)
O(rad)–Ln–O(rad)	137.6(3)	136.9(4)

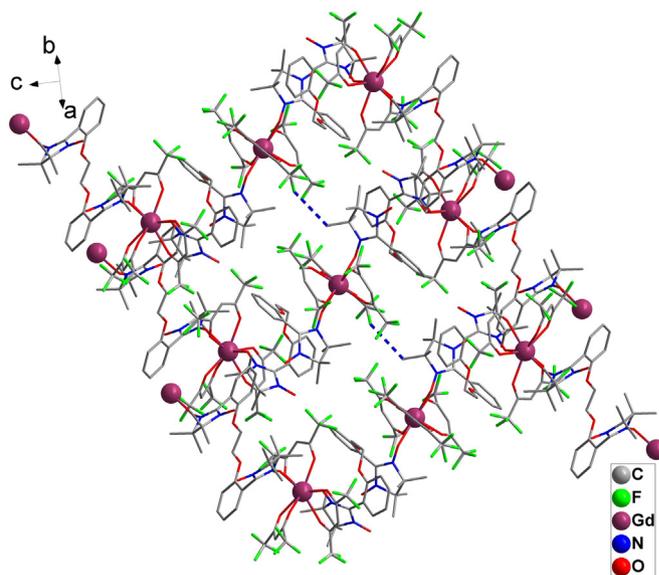
The closest contact between the uncoordinated NO groups are 8.303 Å for **1** and 8.257 Å for **2**. The chains are connected through weak C–H⋯F hydrogen bonds (Table S4), resulting in a 2D supramolecular network for **1** and **2**.

The variable-temperature magnetic susceptibility measurements of complexes **1** and **2** were conducted in the range 2–300 K under an applied magnetic field of 1000 Oe and are shown in Fig. 3 as the $\chi_M T$ vs. T form in which χ_M represents the susceptibility for a formula unit without solvent molecules. At room temperature, the $\chi_M T$ values are 8.83 and 15.29 cm³ Kmol⁻¹ for complexes **1** and **2**, respectively, which are slightly higher than the expected values (8.63 cm³ Kmol⁻¹ for **1**; 14.92 cm³ Kmol⁻¹ for **2**) for uncoupled one Ln^{III} ion (Gd^{III}: ⁸S_{7/2}, $S = 7/2$, $L = 0$, $g = 2$, $C = 7.88$ cm³ Kmol⁻¹; Dy^{III}: ⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$, $C = 14.17$ cm³ Kmol⁻¹) and one biradical (mono radical: $S = 1/2$, $g = 2.0$, $C = 0.375$ cm³ Kmol⁻¹).

For complex **1**, upon cooling, the $\chi_M T$ value is almost constant until 75 K, then increases gradually to reach a maximum of 9.36 cm³ Kmol⁻¹ at 10 K. This behavior is indicative of ferromagnetic interaction. Below 10 K, $\chi_M T$ value decreases quickly to 8.93 cm³ Kmol⁻¹ at 2 K. According to the crystal structure and the reported related Gd–nitronyl nitroxide complexes [18–21], Gd(III)-coordinated NO group magnetic coupling (J_1) and magnetic interaction (J_2) between two NO groups through the Gd(III) ion should dominate in the present magnetic system. The magnetic interaction between two mono-radicals within the biradical is expected to be very weak. Thus, from the view of magnetic point, complex **1** can be regarded as Rad–Gd–Rad tri-spin units and the magnetic data could be analyzed by a theoretical expression deduced from the spin Hamiltonian $H^{\wedge} = -2J_1(\hat{S}_{Gd} \cdot \hat{S}_{Rad1} + \hat{S}_{Gd} \cdot \hat{S}_{Rad2}) - 2$

Fig. 1. (Left) One-dimensional chain of complex **1**, all of the hydrogen and fluorine atoms and hexane solvent molecules are omitted for clarity. (Right) The coordination polyhedron of the Gd ion in complex **1**. Symmetry code: A -x + 4/3, -x + y + 2/3, -z + 1/6.Table 2
SHAPE analysis for complexes **1** and **2**.

Complex	TDD-8	BTPR-8	JSD-8
1 Gd	0.062	2.533	2.545
2 Dy	0.044	2.555	2.528

Fig. 2. 2D packing diagram of **1** through the weak intermolecular interactions: C3–H3B...F8#1 with the distance of 3.30 Å. All of the hydrogen atoms and hexane solvent molecules are omitted for clarity.

$J_2 \hat{S}_{Rad1} \cdot \hat{S}_{Rad2}$. The possible interactions of interchain and two mono-radicals within the biradical are introduced by the mean-field, zJ' .

$$\chi_{Gd} = \frac{Ng^2\beta^2}{4kT} \left[\frac{165 + 84 \exp\left(\frac{-9J_1}{kT}\right) + 84\left(\frac{-7J_1 - 2J_2}{kT}\right) + 35 \exp\left(\frac{-16J_1}{kT}\right)}{5 + 4 \exp\left(\frac{-9J_1}{kT}\right) + 4\left(\frac{-7J_1 - 2J_2}{kT}\right) + 3 \exp\left(\frac{-16J_1}{kT}\right)} \right]$$

$$\chi_M = \frac{\chi_{Gd}}{1 - \left(\frac{2zJ'}{Ng^2\beta^2}\right) \chi_{Gd}}$$

The best fitting resulted in magnetic parameters: $J_1 = 0.65$ cm⁻¹, $J_2 = -2.74$ cm⁻¹, $zJ' = -0.02$ cm⁻¹ and $g = 2.01$. The positive J_1 is in agreement with ferromagnetic interaction between Gd(III) and coordinated the NO group, while the negative J_2 value indicates that there is antiferromagnetic coupling between two NO groups through the

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