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First coordination compounds based on a bis(imino nitroxide) biradical and 4f metal ions: synthesis, crystal structures and magnetic properties

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Abstract

The synthesis, crystal structure and magnetic properties of two families of heterospin complexes containing lanthanide ions and a bis(imino nitroxide) biradical (IPhIN = 1-iodo-3,5-bis(4',4',5',5'-tetramethyl-4',5'-dihydro-1*H*-imidazole-1'-oxyl)benzene) are reported: In [Ln₂(hfac)₆(IPhIN)(H₂O)₂] compounds, two lanthanide ions [Ln = Gd^{III} (**1**) or Dy^{III}(**2**)] are coordinated to the biradical, and in [Ln(hfac)₃(IPhIN)(H₂O)] compounds, one lanthanide ion (Ln = Tb^{III} (**3**), Gd^{III} (**4**) and Dy^{III} (**5**)) is coordinated to the biradical. Ferromagnetic intramolecular magnetic interactions between Gd^{III} and the biradical were found for **1** and **4**, while intramolecular magnetic interactions between the radicals were ferro- and antiferromagnetic, respectively. Compound **2** shows a field induced slow relaxation of magnetization, which (under an external applied field of 2 kOe) exhibits an activation energy barrier of $\Delta E/k_B = 27$ K and a pre-exponential factor of 1.4×10^{-8} s. To support the magnetic characterization of compound **3** *ab initio* calculations were also performed.

1) Introduction

The use of stable organic radicals as building blocks is a well-established strategy towards designing new molecular magnetic compounds,¹ and a new burst of interest arose after the discovery of single chain magnet behavior in a heterospin system containing an organic radical coordinated to a metal ion.²⁻³ Although much effort has been made using the nitronyl nitroxide and nitroxide (aminoxyl) *monoradical* units, the use of organic *biradicals* is relatively less explored. The latter are very appealing because the intramolecular magnetic exchange interactions between two radical moieties can be designed and widely tuned within the same biradical unit by choosing an appropriate conjugated spacer to link the radical spins. This allows wider control of the magnetic properties of a metal-radical system than can be achieved using simpler monoradicals.

Recently, some of us reported metal-radical systems containing a bis(imino nitroxide) biradical.⁴ A major reason for exploring use of this biradical is that it has four coordination sites: two oxygens and twoazole nitrogen donors from nitroxide and imidazole moieties, respectively. These distinguishable coordinating sites can give rise to a large variety of heterospin complexes. Among the possibilities, lanthanide ions are particularly good choices for coordination compounds, because of their large uniaxial magnetic anisotropy and large magnetic moments that could exhibit magnetic hysteresis due to slow relaxation of the magnetization. This magnetic behavior is observed in single molecule magnets (SMM), single chain magnets (SCM) and more recently single ion magnets (SIM).^{2,5} These types of compounds are being intensively studied due to their potential application in high-density data storage materials and quantum computations, as well as to understand their unusual magnetic quantum behaviors.⁶ Much effort has been expended to increase the blocking temperatures of slow relaxing magnetic systems,⁷ and lanthanide-based coordination compounds are very promising due to their large magnetic anisotropy.⁸ Some coordination compounds containing organic bis(nitronyl nitroxide) ligands exhibiting slow magnetic relaxation have been reported.^{9,10,11} However, to our knowledge there are no reported examples of lanthanide-

based coordination compounds with bis(imino nitroxide) ligands. Therefore, we focused on the coordination of block-*f* metal ions using the bis(imino nitroxide) biradical previously used by some of us -- 1-iodo-3,5-bis(4',4',5',5'-tetramethyl-4',5'-dihydro-1*H*-imidazole-1'-oxyl)benzene (IPhIN) -- for coordination with non-lanthanide metals.⁴ Herein, we report the synthesis, crystal structure and magnetic properties of two families of heterospin complexes containing lanthanide ions and the IPhIN biradical. The first family consists of dinuclear units with general formula $[\text{Ln}_2(\text{hfac})_6(\text{IPhIN})(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Gd}^{\text{III}}$ (**1**) and Dy^{III} (**2**)), in which the metal ions are bridged by the IPhIN. In the second one, the IPhIN radical is monocoordinated to $\{\text{Ln}(\text{hfac})_3\}$ units leading to mononuclear species $[\text{Ln}(\text{hfac})_3(\text{IPhIN})(\text{H}_2\text{O})]$ ($\text{Ln} = \text{Tb}^{\text{III}}$ (**3**), Gd^{III} (**4**) and Dy^{III} (**5**)). The magnetic properties were investigated and the data treated using models that consider two exchange couplings in order to take into account the metal-radical and radical-radical (intramolecular) magnetic exchange. CASSCF/RASSI-SO *ab initio* calculations were performed to support the magnetic interpretation. Compound **2** displays slow relaxation of its magnetization.

2) Experimental Section

2.1) General procedures

All reagents and solvents were purchased from commercial sources and used without additional purification. The $[\text{Ln}(\text{hfac})_3]$ ($\text{Ln} = \text{Gd}^{\text{III}}$, Dy^{III} and Tb^{III}) and IPhIN building blocks were synthesized as described elsewhere.^{4,12}

2.2) Synthesis of complexes 1-5

A suspension containing 0.12 mmol of an appropriate $[\text{Ln}(\text{hfac})_3]$ hydrate ($\text{Ln} = \text{Gd}^{\text{III}}$ (**1** and **4**), Dy^{III} (**2** and **5**) or Tb^{III} (**3**)) in 20 mL of *n*-heptane was boiled until dissolution. Then, 0.021 g (0.06 mmol) of IPhIN dissolved in 2 mL of CHCl_3 was added with stirring. The solution was kept at 10 °C, and after 10 days pale pink prism (**1-2**) or dark violet block (**3-5**) crystals were obtained. Single

crystals were manually separated from the mother liquor to maintain maximum purity: these were washed with *n*-heptane, and dried in air. For [Ln(hfac)₃·*n*H₂O] where Ln = Gd and Dy, two types of crystals were always observed in the final product, even when the reactant stoichiometry was varied. Powder X-ray diffraction patterns for **1**, **2**, **4** and **5** were compared with the simulated powder diffraction pattern predicted from the crystal structure. The experimental and simulated peaks corresponded well in position and relative intensity, confirming the phase purity of the compounds separated manually (see supporting information for details, Fig. S1 and S2).

Compound (1): Analysis calculated for C₅₀H₃₇F₃₆Gd₂IN₄O₁₆ C 28.94, H 1.80, N 2.70; Found C 29.05, H 2.15, N 2.56; IR (ATR, ν cm⁻¹): 3353 (b, O-H), 3197 (w, C-H aromatic), 2996, 2962 (w, C-H aliphatic), 1647 (s, C=O); 1252, 1194, 1133, 1095 (s, C-F).

Compound (2): Analysis calc. for C₅₀H₃₇F₃₆Dy₂IN₄O₁₆ C 28.79, H 1.80, N 2.69; Found C 28.62, H 2.07, N 2.99; IR: 3343 (b, O-H), 3050 (w, C-H aromatic), 2960, 2920 (w, C-H-aliphatic), 1651 (s, C=O), 1249, 1191, 1136, 1097 (s, C-F).

Compound (3): Analysis calc. for C₃₅H₃₂F₁₈IN₄O₉Tb C 32.83, H 2.52, N 4.38; Found C 32.56, H 2.37, N 4.51; IR: 3341 (b, O-H), 3082 (w, C-H aromatic), 2989, 2932 (w, C-H aliphatic), 1654 (s, C=O), 1251, 1194, 1137, 1102 (s, C-F).

Compound (4): Analysis calc. for C₃₅H₃₂F₁₈IN₄O₉Gd C 32.83, H 2.52, N 4.38; Found C 33.10, H 2.98, N 4.35; IR: 3341 (b, O-H), 3147 (w, C-H aromatic), 2979 (w, C-H aliphatic), 1649 (s, C=O), 1252, 1194, 1134, 1096 (s, C-F).

Compound (5): Analysis calc. for C₃₅H₃₂F₁₈IN₄O₉Dy C 32.74, H 2.51, N 4.36; Found C 32.77, H 2.62, N 4.27; IR: 3427 (w, O-H), 3146 (w, C-H aromatic), 2980 (w, C-H aliphatic), 1649 (s, C=O), 1252, 1194, 1135, 1098 (s, C-F).

2.3) X-ray diffraction

Powder X-ray diffraction data for all samples were collected on a Bruker D8 Advance equipped with a Lyn-xEye detector. Single crystal X-ray data were collected on an Oxford GEMINI A Ultra diffractometer for **1-3** at 120 K and on a Bruker D8 Venture diffractometer for **4-5** at 150 K and 293 K, respectively, using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, data reduction, cell refinement and absorption corrections for **1-3** were performed using the CrysAlis RED software, Oxford Diffraction Ltd., Version 1.171.32.38. For **4-5**, data collection and cell refinement were performed using Bruker Instrument Service v4.2.2 software and APEX2,¹³ respectively. Data reduction was carried out using SAINT.¹⁴ Empirical multiscan absorption correction using equivalent reflections was performed using the SADABS program.¹⁵ The final crystal structures were solved using SHELXS-97 software, and structure refinement was performed using SHELXL-97 software based on F^2 through full-matrix least squares routines.¹⁶ All atoms except hydrogen were refined anisotropically. The H-atoms were treated by a mixture of independent and constrained refinement. Crystals of **4** had limited quality and the crystal structure could not be refined well (see supporting information for details). Details of data collection and structure refinement for compounds **1-3** and **5** are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1

2.4) Magnetic measurements

Dc magnetic measurements were carried out using a Cryogenic Sx600 SQUID magnetometer for compounds **1-4** and a Quantum Design MPMS XL-7 SQUID magnetometer for compound **5**. Freshly prepared single crystals were placed in a gelatin capsule. The crystals of **2**, **3** and **5** were first wrapped in polytetrafluoroethylene tape and pressed into a pellet in order to prevent field orientation of the crystals during measurement. Ac measurements were performed with a Quantum

Design PPMS using the same samples used for dc measurements. Magnetic data were corrected for diamagnetic contributions of the sample and the sample holder.

2.5) *Ab Initio Calculations for compound 3*

Ab initio calculations for compound **3** were carried out using structure obtained from the experimental single-crystal X-ray diffraction analysis. With all other atom positions fixed, the positions of the hydrogen atoms and disordered fluorine atoms were optimized using the program GAUSSIAN 09¹⁷: Stuttgart/Dresden energy-consistent pseudopotentials (ECP's) and relative double zeta polarized basis sets¹⁸ with the PBE0 functional¹⁹ were employed.

The resulting geometry was used to compute the isotropic magnetic exchange coupling between radical spin units and the Tb^{III} ions, complete active space self-consistent field (CASSCF) calculations were performed *without* spin-orbit contributions. These were performed with the MOLCAS 8.1 Quantum Chemistry Software Package²⁰. The active space consisted of the 7 *f*-orbitals of the terbium ion and the π^* type radical orbitals (where much of the unpaired electron density of the two radical units are localized) for a total of 10 electrons in 9 active orbitals, *i.e.* CAS(10,9).

Spin orbit coupling effects were then evaluated by computing *g*-tensor elements of the main magnetic anisotropy axis of Tb^{III} in compound **3**, using the SINGLE_ANISO module in MOLCAS. Table S3 in the supporting material shows the computed energy levels for the Tb^{III} ion obtained from state average restricted active space state interaction (RASSI) calculations with inclusion of spin-orbit coupling, the CASSCF/RASSI-SO method. These energy states were computed by “doping” the organic biradical unit with two extra electrons to make it a diamagnetic ligand. Because the organic ligand was rendered closed-shell diamagnetic, the active space became 8 electrons in the 7 *f*-orbitals of terbium ion, CAS(8,7). Due to computational resource limitations, only the resultant seven septuplet states were considered and included in the spin orbit calculation.

3) Results and discussion

3.1) Crystal structures

3.1.1) U-shaped dinuclear complexes

Figure 1

Compounds **1** and **2** crystallize in the triclinic *P*-1 space group, and are isomorphous with only slight differences in the crystal packing. The molecular unit is shown in Fig. 1, and consists of dinuclear species in which each lanthanide(III) ion [Gd (**1**) or Dy (**2**)] has a bicapped trigonal prismatic geometry coordinated by three hfac⁻ ligands, one IPhIN nitroxide moiety, and one water molecule. Selected bond distances and angles are gathered in Table 2. The Ln-O_{hfac} bond lengths are 2.332(6)-2.442(7)Å (in **1**) and 2.307(9)-2.37(1)Å (in **2**), while the Ln-O_{water} bond lengths are 2.381(5) (Gd1-O8) and 2.377(5)Å (Gd2-O16) for **1**, and 2.35(1) and 2.36(1)Å for Dy1-O8 and Dy2-O16 for **2**. The IPhIN biradical acts as a bridging ligand between two {Ln(hfac)₃(H₂O)} units. Although IPhIN has two imidazole nitrogen atoms available for coordination, each lanthanide ion is preferentially coordinated by the nitroxide oxygen atoms. The Ln-O_{nitroxide} bond lengths are 2.379(5) and 2.353(7)Å for Gd1-O1 and Gd2-O9 in **1**, and 2.331(9) and 2.35(1) Å for Dy1-O1 and Dy2-O9 in **2**. These bond lengths are in agreement with other gadolinium(III) and dysprosium(III) complexes having lanthanides coordinated by nitroxides.^{21,22} The Ln1-O1-N1 and Ln2-O9-N3 bond angles are much closer to each other for **1**, 133.4(4)° and 133.5(8)°, than the analogous bond angles in isomorphous **2**, 137.7(4) and 135(1)°, respectively. One of the biradical conformational torsion angles was almost coplanar with the central *m*-phenylene ring, with ∠N1—C1—C2—C7 -2(1)° in (**1**) and -2(3)° in (**2**), whereas the other ring was significantly twisted with ∠N3—C8—C6—C7 torsion angles of 36(1)° and -35(3)° for **1** and **2**, respectively. Despite this difference, the M-ON coordination sites on the biradical are aligned in the same direction and are *syn* to one another at a

fairly close distance. Intramolecular hydrogen bonding between coordinated water molecules and hfac^- moieties is also observed: in compound **2**, the hydrogen bonding for O8 and O16 is bifurcated. These hydrogen bonds probably assist the formation of the molecular U-shaped framework (see Table S1 for geometry parameters), to give the short $\text{Ln1}\cdots\text{Ln2}$ distances across the *m*-phenylene unit of 5.7967(8) Å for **1** and 5.778(1) Å for **2**. The intermolecular crystal packing of **1** is further stabilized by $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{F}$ interactions, while $\text{F}\cdots\text{F}$ and $\text{C}_{\text{sp}^3}\text{-H}\cdots\text{F}$ short contacts are observed in **2**.

Table 2

3.1.2) Mononuclear complexes

Complexes **3**, **4** and **5** are also isomorphous, and crystallize in the monoclinic $P2_1/c$ space group. Due to the low quality of crystals of **4** (see Table S2 -ESI), we focus here on the crystal structures of **3** and **5**. These are mononuclear complexes, in which the lanthanide ion (Tb^{III} , **3** or Dy^{III} , **5**) is octacoordinated by three hfac^- ligands, one IPhIN radical and one water molecule, lying on a bicapped trigonal prismatic environment. The $\text{Ln-O}_{\text{hfac}}$ bond distance ranges from 2.343(5) to 2.392(5) Å in **3** and from 2.350(14) to 2.378(10) Å in **5**, while the $\text{Ln-O}_{\text{water}}$ bond lengths are 2.422(5) (3) and 2.387(12) Å (5). In contrast with compounds **1** and **2**, the IPhIN biradical acts as a monodentate ligand towards the metal ion for **3** and **5** as shown in Fig. 2. Due to the oxophilic character of the lanthanide ion, the imidazole nitrogen atoms are not coordinated, similarly to the situation for **1** and **2**. This coordination mode adopted by the IPhIN biradical was also previously observed with cobalt(II) and manganese(II) complexes, where only the oxygen atom of the imino nitroxide moiety is coordinated to the metal ions.⁴ The $\text{Ln-O}_{\text{nitroxide}}$ bond lengths are 2.275(4) and 2.270(9) Å, for **4** and **5**, respectively. The $\text{Dy-O}_{\text{nitroxide}}$ bond length in **5** is slightly shorter than the corresponding bond in **2**. The $\text{Tb-O}_{\text{nitroxide}}$ bond length in **3** is slightly shorter than for other terbium(III) compounds coordinated by a nitroxide oxygen atom previously reported in the

literature.^{10,11,22} The Ln1-O1-N1 bond angle is slightly larger in **5** [137.9(7)°] when compared with that observed for **3** [135.8(3)°]. The torsion angles between the imidazole and phenyl rings are larger than corresponding angles in **1** and **2**, revealing that monocoordination of IPhIN biradical allows it to have more structural flexibility compared with dinuclear coordination. The torsion angles between the imidazole and phenyl rings are larger for **3** ($\angle\text{N1-C1-C2-C3} = 29.8(9)^\circ$ and $\angle\text{N3-C8-C6-C7} = 152.7(6)^\circ$) and **5** ($\angle\text{N1-C1-C2-C3} = -149(1)^\circ$ and $\angle\text{N3-C8-C6-C7} = 153(1)^\circ$) than those found for **1-2**.

It is noteworthy that previous work has shown that the torsion angle of radical units relative to a connecting *m*-phenylene ring in similar biradicals can influence magnetic properties, particularly the intramolecular exchange interaction between radical units.²³ This is important, because the IPhIN ligand adopts a coordination mode where each oxygen atom from nitroxide groups is coordinated to (at most) one lanthanide ion. This situation is different from some previously reported lanthanide-based compounds coordinated by bis(nitronyl nitroxides), where oxygen atoms of *both* radical units are coordinated to the same ion, adopting a chelating mode.¹⁰⁻¹¹ The multiple conformational possibilities for coordination in the present case with IPhIN, allows more complexity. For example, the nitroxide moieties (coordinated and uncoordinated) in **3** are oriented in *opposite* directions, supporting a key structural role for its intramolecular hydrogen bonds involving water ligands and uncoordinated imidazole nitrogen atom, as shown in Fig. 3. Quite short contacts between the uncoordinated nitroxide oxygen atom (O9) and the neighboring imidazole nitrogen atom (N2ⁱ, *i* = -*x*, -*y*, -*z*) form at a distance of only 2.926(7) Å for compound **3** in (Fig. 3). But, for these monocoordinate systems, the closest Ln^{III}Ln distances are very long, 13.4039(5) Å in **3** and 13.298(1) Å in **5**. The IPhIN *m*-phenylene spacer forms π - π stacks (Fig. 3) with centroid-to-centroid distances and the slip-stacking angles (4.14 Å and 22.5° for **3**, and 4.06 Å and 22.5° for **5**) that are consistent with other reported values for related structures.²⁴

Figures 2 and 3

3.2) Magnetic properties

The magnetic properties were investigated in the temperature range 2-290 K for **1-3** and in the temperature ranges 2-240 K and 6.4-300 K for **4** and **5**, respectively. The plots of the product of magnetic molar susceptibility with temperature ($\chi_M T$) versus temperature (T) are shown in Figs. 4 and 5 for the dinuclear **1-2** and mononuclear **3-5** complexes, respectively. At high temperature the values of $\chi_M T$ are 16.6, 29.0, 12.5, 8.5 and 14.3 cm³·mol⁻¹·K for compounds **1-5**, respectively: these values are very close to those expected (16.5, 29.1, 12.6, 8.6 and 14.9 cm³·mol⁻¹·K) for uncoupled spins. More detailed analyses of the magnetism are given below for the two types of structure.

3.2.1) U-shaped dinuclear complexes **1-2**

Figure 4

For compound **1**, $\chi_M T$ remains relatively constant upon cooling, and then increases at lower temperatures, indicating predominant ferromagnetic interactions among the spin carriers. Attempts to reproduce the magnetic data considering only interactions between Gd^{III} ions and isolated radical units were not fruitful, showing the necessity to account for magnetic interaction between spins of the biradical. Therefore, two isotropic exchange interactions were used in a model spin Hamiltonian (Eq. 1) to consider respectively the interaction between Gd^{III} ions and radicals (J_1), and between the radicals in the biradical unit (J_2). Although the Gd1^{III}-Gd2 distance is rather short in the molecular U-shaped framework, this magnetic dipolar interaction should be quite small, and to avoid overparameterization it was not considered.

$$\hat{H} = -J_1(\vec{S}_{Gd1} \cdot \vec{S}_{Rad1} + \vec{S}_{Gd2} \cdot \vec{S}_{Rad2}) - J_2(\vec{S}_{Rad1} \cdot \vec{S}_{Rad2}) + g\mu_B B[\vec{S}_{Rad1} + \vec{S}_{Rad2} + \vec{S}_{Gd1} + \vec{S}_{Gd2}] \text{ (Eq. 1)}$$

The magnetic data were fitted using the MagProp routine in the DAVE software suite.²⁵ The solid line in Fig. 4 shows the best fit parameters found for **1**: $g = 1.99 \pm 0.01$, $J_1 = 0.3 \pm 0.1 \text{ cm}^{-1}$ and $J_2 = 6.5 \pm 2.7 \text{ cm}^{-1}$ with $S_{Gd1} = S_{Gd2} = 7/2$, and $S_{Rad1} = S_{Rad2} = 1/2$. The obtained Gd^{III}-Rad[•] coupling constant J_1 lies within the range observed for related compounds.²⁶ Recent magneto-structural studies have found a strong relation between the Gd^{III}-Rad[•] exchange coupling and the torsion angle Gd-O-N-C.²⁷ Ferromagnetic exchange is favored for large torsion angles like those in compound **1**, where Gd1-O1-N1-C1 = 82(1)° and Gd2-O9-N3-C8 = 115.1(7)°. In addition, with respect to exchange between the biradical spins, the dihedral angle between the imidazole ring and the *m*-phenylene unit plays a key role for exchange coupling J_2 .²³ For **1**, the inter-ring dihedral angles are not large, which is expected to give ferromagnetic inter-radical exchange coupling J_2 , consistent with the fitted result.

For compound **2**, $\chi_M T$ remains constant down to 90 K then decreases at lower temperatures. For compounds containing lanthanide ions other than Gd^{III}, depopulation of the crystal-field split M_J states (Stark sublevels) is especially important in magnetic behavior. Since depopulation of the Stark sublevels occurs simultaneously with possible magnetic exchange interaction and magnetic anisotropy effects, it is very difficult to model the magnetic behavior to quantify Dy-radical and intra-biradical (radical-radical) exchange interactions separately.²⁸ Nevertheless, since the crystal structure of **2** is quite similar to that for **1**, with comparable torsion angles for Dy-radical interaction, and radical-radical interaction across *m*-phenylene, the nature of the magnetic exchanges is expected to be the same, i.e., both ferromagnetic. Plots of M vs. H/T data obtained at different temperatures do not superimpose on a single master curve for **2** (Fig. S3 in SI). Moreover, the molar magnetization value of 11.9 N β at 62.5 kOe is low compared to the expected saturation for **2**. Because the expected exchange is ferromagnetic, but the magnetic moment is low, significant magnetic anisotropy and/or low-lying excited states appear to contribute to the magnetism of **2**.

3.2.2) Mononuclear complexes 3 – 5

Figure 5

For compound **4**, as temperature decreases, $\chi_M T$ increases to a maximum of $9.1 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 6.4 K, then decreases to $8.7 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2.6 K, indicating the coexistence of ferro- and antiferromagnetic exchange interactions. These magnetic susceptibility data were fitted using a model spin Hamiltonian (Eq. 2) very similar to the one used for compound **1**, but with only one Gd^{III} ion. The intermolecular magnetic interactions between the molecular units through the $\text{O9} \cdots \text{N2}^{\text{i}}$ short contact are expected to be sufficiently weaker to be ignored in the model; this is also important to prevent overparametrization.

$$\hat{H} = -J_1(\vec{S}_{\text{Gd1}} \cdot \vec{S}_{\text{Rad1}}) - J_2(\vec{S}_{\text{Rad1}} \cdot \vec{S}_{\text{Rad2}}) + g\mu_B B[\vec{S}_{\text{Rad1}} + \vec{S}_{\text{Rad2}} + \vec{S}_{\text{Gd1}}] \quad (\text{Eq.2})$$

Fitting was performed using the aforementioned software to give the best fit parameters: $g = 1.99 \pm 0.01$, $J_1 = 1.4 \pm 0.5 \text{ cm}^{-1}$ and $J_2 = -3.9 \pm 0.7 \text{ cm}^{-1}$ with $S_{\text{Gd1}} = 7/2$, and $S_{\text{Rad1}} = 1/2$. The metal-radical magnetic coupling constant lies within the range found for other systems having Gd^{III} -radical bonding.²⁶ However, with respect to the radical-radical interaction within the biradical, ferromagnetic interactions are usually found within 1,3-phenylene linked biradicals when the torsion angle between the *m*-phenylene spacer and imidazole rings is less than 60° . Just such a ferromagnetic interaction was observed in compound **1** with its modest radical-to-phenylene torsion.²³ It is known that metal ions can influence the structural conformation of ligands leading to different intramolecular magnetic interactions between radicals.¹⁰ In our systems, differences between the mononuclear and dinuclear complexes occur with respect to the torsion angles between imidazole and phenyl rings within the biradical unit. Indeed, these two phenylene-radical torsion angles are quite different for the dinuclear compounds ($\sim 2^\circ$ and $\sim 35.5^\circ$) but quite similar for the mononuclear ones ($\sim 28^\circ$ and $\sim 30^\circ$). Although the dihedral angles in compound **4** are not so large as would be expected to induce antiferromagnetic interaction between radicals in an *uncomplexed*

biradical²³, still an antiferromagnetic intra-biradical exchange interaction appears to be present in **4** and it does have more total radical to phenylene torsion than in **1**. Possibly there is also some contribution to the overall downturn of the $\chi_M T$ versus T plot from antiferromagnetic exchange across the O9^{···}N2ⁱ short contacts.

For compounds **3** and **5**, $\chi_M T$ decreases upon cooling temperature down to 11.0 and 13.2 cm³·mol⁻¹·K respectively. As described for compound **2**, the depopulation of the excited M_J states together with possible magnetic exchange interactions and/or anisotropy precludes separate determination of these magnetic contributions. Nevertheless, since compounds **3** and **5** are isomorphous with **4**, including similar values of the characteristic torsion angles aforementioned, the same nature of magnetic metal-radical and intra-biradical (radical-radical) couplings is expected, *i.e.*, ferromagnetic and antiferromagnetic exchange, respectively. The isothermal field dependencies of the magnetization were measured for **3** at different temperatures and do not superimpose. Therefore, the low molar magnetization values of 6.3 N β and 6.5 N β at 62.5 kOe that are observed for compounds **3** and **5**, respectively, indicate significant magnetic anisotropy and/or low-lying excited states (Fig. S4 and S5 in SI).

To support the reliability of the experimental exchange couplings, we also performed post-Hartree-Fock *ab initio* calculations to model the behaviour of compound **3**, which was chosen due to its less disordered crystal structure. Indeed, magnetic properties are very sensitive to the structural parameters and, therefore, in presence of tiny magnetic interactions a reliable geometry is mandatory. The exchange constants J_1 and J_2 (see eq. 2) were computed from CASSCF energies of the lowest nonuplet, sextuplet, and quartet states of an appropriate biradical-Tb model structure. A ferromagnetic interaction of 0.4 cm⁻¹ for the Tb^{III}-radical interaction was computed, with an intra-radical antiferromagnetic interaction of -2.8 cm⁻¹. The value for J_2 fits the behavior of compound **4** (which should not be complicated by spin-orbit coupling), while J_1 is qualitatively correct in being ferromagnetic, but with a predicted magnitude much at variance with experiment. Clearly the

calculation of exchange couplings considering spin-orbit coupling is problematic for ions like Tb^{III}, even qualitatively.²⁹

To have better insight into the magnetic structure of the lanthanide ion in **3**, State Average CASSCF/RASSI-SO computations that include spin-orbit effects were performed. Indeed, although Tb^{III} is a non-Kramer ion, the ground spin-orbit state and first excited state are quasi-degenerate (see supporting material Table S4) with an energy gap around 0.3 cm⁻¹ and a similar composition in terms of spin-free functions. Therefore these two states form an Ising doublet with a small intrinsic gap³⁰. Its magnetic properties were investigated inside the pseudospin framework and its anisotropy axes were calculated using a pseudospin $S = \frac{1}{2}$. The main values of the g tensor calculated on the basis of the two lowest states (supporting material Table S5) reveal a pure Ising-type local magnetization on the Tb^{III} ion in agreement with the experimental magnetic data. These are shown pictorially in Figure 6, along with the predicted magnetic easy axis.

Figure 6

3.2.3) Dynamic Magnetic Properties of **2**.

The dynamic properties of compound **2** were investigated by temperature and frequency dependent ac magnetic susceptibility measurements in the range 2.4-15 K at 10 Hz-10 kHz. In absence of dc field, the thermal dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities is shown in Fig. S6 in SI for **2**. The compound clearly exhibits slow relaxation of magnetization, with frequency dependence for both in-phase (χ') and out-of-phase (χ'') susceptibilities: however no maxima were observed down to 2.4 K.

Figure 7

It is well known that for SMM and SIMs, the fast quantum tunneling of the magnetization (QTM) occurring at resonance fields, mainly in zero field, can be hampered by a nonzero external field. Therefore, the ac susceptibilities were also measured under a static external magnetic field, which shifted the frequency dependence curves to higher temperatures. This behavior is a characteristic signature that QTM is occurring at zero magnetic field. For external field $H_{ext} = 2$ kOe, compound **2** exhibits frequency-dependent maxima for both in-phase and out-of-phase susceptibilities (Fig. 7). The relaxation times obtained from the temperature dependence of the out-of-phase susceptibility maximum were fitted to an Arrhenius law (see supporting material Fig. S7), to give an energy barrier of $\Delta E/k_B = 27$ K with a pre-exponential factor $\tau_0 = 1.4 \times 10^{-8}$ s. Furthermore, the value of the relative variation of χ' peak temperature (T_f) per decade frequency (ν) ($K = \Delta T_f / [T_f \Delta(\log \nu)]$) is 0.24, which is analogous to behavior seen in superparamagnets and SMMs (0.28).³¹

The shape of the in-phase magnetic susceptibilities at low temperatures, as well as the broad out-of-phase peaks, are consistent with a distribution of relaxation times. Therefore, isothermal ac susceptibility measurements were performed while varying the ac frequency at different temperatures in a fixed external field of 2 kOe (Fig. S8), and the relaxation distribution width α was calculated by the Debye formula.³² At lower temperatures, the distribution broadens drastically, with α increasing from 0.17 at 8 K to 0.57 at 2.4 K. Taken together with the shapes of the in-phase magnetic susceptibilities at low temperature, this large increase of the distribution width suggests more than one relaxation process, which is consistent with the presence of two distinct Dy^{III} ion environments in the crystal structure of compound **2**. Unfortunately, due to the lack of distinctly differentiated peaks in the relaxation data at 2 kOe, any fitting attempt using two relaxation processes results in overparametrization with no reliably independent parameters.

4) Conclusion

We synthesized and characterized two novel families of heterospin complexes containing lanthanide ions and a bis(imino nitroxide) biradical: one with two lanthanide ions coordinated to one biradical moiety, and the other with one lanthanide ion coordinated to the biradical. Ferromagnetic intramolecular magnetic interactions between Gd^{III} and the biradical were found for **1** and **4**, with intramolecular interactions between the radicals being ferro- or antiferromagnetic, respectively. *Ab initio* calculations supported the nature of the magnetic coupling constant obtained experimentally from the Gd^{III} complexes, and predicted the magnetic anisotropy axis elements for Tb^{III} in compound **3**. Compound **2** shows a field dependent slow relaxation of the magnetization consistent with SMM type behavior. Since the nitrogen atoms of IPhIN are not coordinated to any metal ion, **1-5** can be further used as building blocks to synthesize heterometallic compounds, using metal ions that coordinate preferably to nitrogen donor atoms such as first row transition metal ions.

5) Acknowledgments

Financial support from Brazilian agencies FAPERJ, CAPES, CNPq, and the Science without Borders Program (Special Visiting Researcher – 400808/2012-9), are gratefully acknowledged. We also acknowledge LDRX-UFF (Universidade Federal Fluminense, Brazil), LabCri (Universidade Federal de Minas Gerais, Brazil), Prof. Miguel A. Novak, Prof. Luis Ghivelder from IF-UFRJ and Dr. Kleber Pirota (IFGW-UNICAMP) for use of laboratory facilities. Dr. Federico Totti acknowledges Prof. Roberta Sessoli for the fruitful discussions.

6) Supporting Information

Crystallographic data for compounds **1-3** and **5** in CIF format are available as CCDC-No. 1404060-1404062 and 1424570, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Geometry parameters

associated with hydrogen bonding for compounds **1-3** are listed in Table S1. A summary of crystal structure, data collection and refinement is compiled in Table S2. Fig. S3-S5 show the field dependence of the magnetization for compound **2**, **3** and **5**. Ac magnetic data, Arrhenius and Cole-Cole plots for **2** are shown in Fig. S6-S8.

Table 1. Summary of crystal data, collection and refinement parameters for compounds **1-3** and **5**.

Compound reference	(1)	(2)	(3)	(5)
Chemical formula	C ₅₀ H ₃₇ F ₃₆ Gd ₂ IN ₄ O ₁₆	C ₅₀ H ₃₇ F ₃₆ Dy ₂ IN ₄ O ₁₆	C ₃₅ H ₃₂ F ₁₈ IN ₄ O ₉ Tb	C ₃₅ H ₃₂ F ₁₈ IN ₄ O ₉ Dy
Formula Mass	2075.24	2085.74	1280.48	1284.05
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
<i>a</i> /Å	12.5796 (6)	12.5244 (8)	15.2202 (4)	15.2921 (9)
<i>b</i> /Å	13.3674 (5)	13.2968 (9)	12.2385 (3)	12.4066 (8)
<i>c</i> /Å	23.2909 (13)	23.3803 (16)	25.4334 (7)	26.1003 (17)
α /°	89.610 (4)	89.620 (6)	90	90
β /°	83.439 (4)	83.290 (6)	99.026 (3)	99.137 (2)
γ /°	64.895 (4)	65.009 (7)	90	90
Unit cell volume/Å ³	3519.5 (3)	3501.0 (5)	4678.9 (2)	4889.0 (5)
Temperature/K	120	120	120	293
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	2	4	4
Radiation type	MoK α	MoK α	MoK α	MoK α
μ /mm ⁻¹	2.47	2.72	2.30	2.28
Reflections measured	27378	17967	31832	42345
Independent reflections	12415	12352	8273	8653
R_{int}	0.051	0.076	0.042	0.031
R_I values ($I > 2\sigma(I)$)	0.055	0.082	0.05	0.124
$wR(F^2)$ values ($I > 2\sigma(I)$)	0.126	0.208	0.120	0.279
R_I values (all data)	0.081	0.129	0.063	0.135
$wR(F^2)$ values (all data)	0.146	0.260	0.128	0.272
Goodness of fit on F^2	1.03	1.03	1.04	1.07
CCDC Deposition	1404060	1404061	1404062	1424570

Table 2. Selected bond lengths (Å) and bond angles for compounds **1-3** and **5**.

Atom labels	(1) (Ln=Gd)	(2) (Ln=Dy)	(3) (Ln=Tb)	(5) (Ln=Dy)
Ln1—O1	2.379(5)	2.331(9)	2.275(4)	2.270(9)
Ln1—O2	2.385(5)	2.35(1)	2.348(5)	2.350(14)
Ln1—O3	2.381(5)	2.37(1)	2.382(5)	2.378(10)
Ln1—O4	2.375(7)	2.34(1)	2.343(5)	2.351(12)
Ln1—O5	2.386(4)	2.351(9)	2.371(5)	2.365(12)
Ln1—O6	2.349(5)	2.307(9)	2.369(4)	2.373(11)
Ln1—O7	2.442(7)	2.41(1)	2.392(5)	2.39(6)
Ln1—O8	2.381(5)	2.35(1)	2.422(5)	2.387(12)
Ln2—O9	2.353(7)	2.35(1)		
Ln2—O10	2.390(5)	2.342(9)		
Ln2—O11	2.373(4)	2.34(1)		
Ln2—O12	2.332(6)	2.33(1)		
Ln2—O13	2.348(7)	2.32(1)		
Ln2—O14	2.359(6)	2.33(1)		
Ln2—O15	2.428(5)	2.37(1)		
Ln2—O16	2.377(5)	2.36(1)		
N1—O1	1.351(7)	1.34(1)		
N3—O9	1.338(9)	1.32(2)		
Ln1—O1—N1	133.4(4)	133.5(8)	135.8(3)	137.9(7)
Ln1—O9—N3	137.7(4)	135(1)		
N1—C1—C2—C7	-2(1)	-2(3)	29.8(9)	-149(1)
N3—C8—C6—C7	36(1)	-35(3)	152.7(6)	153(1)
Ln1—O1—N1—C1	82(1)	-118(1)	72.8(7)	
Ln2—O9—N3—C8	115.1(7)	-84(2)	-	

CAPTIONS TO FIGURES

Fig. 1: Molecular structure of compounds **1** (Gd^{III}) and **2** (Dy^{III}). Hydrogen atoms, trifluoromethyl and methyl groups were omitted for the sake of clarity.

Fig. 2: Molecular structure of compounds **3** and **5**. Hydrogen atoms and trifluoromethyl groups were omitted for the sake of clarity.

Fig. 3: Details of the crystal packing of compounds **3** and **5**, highlighting the N_{imidazole}...O_{nitroxide} short contacts and π - π stacking between *m*-phenylene rings. Hydrogen atoms, methyl and trifluoromethyl groups were omitted for the sake of clarity.

Fig. 4: Thermal dependence of $\chi_M T$ for **1**(□), **2**(○) at $H_{\text{external}}=1$ kOe. The solid line represents the best fit for **1** using the model of Eq. 1.

Fig. 5: Thermal dependence of $\chi_M T$ for **3**(Δ), **4**(□) and **5**(○) at $H_{\text{external}}=1$ kOe. The solid line represents the best fit for **4** using the model of Eq.2.

Fig. 6: Orientation of the calculated magnetic easy axis (blue bar) of the ground quasi-doublet in the molecule of **3**.

Fig. 7: Thermal dependence of the in-phase and out-of-phase susceptibility components for compound **2** at $H=2$ kOe.

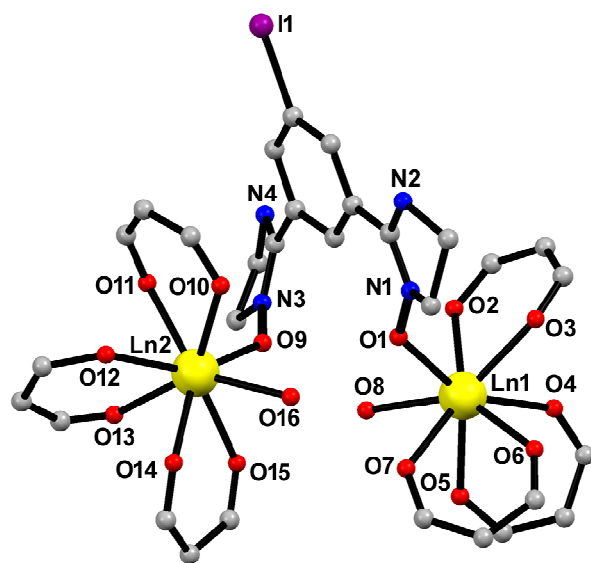


Fig. 1

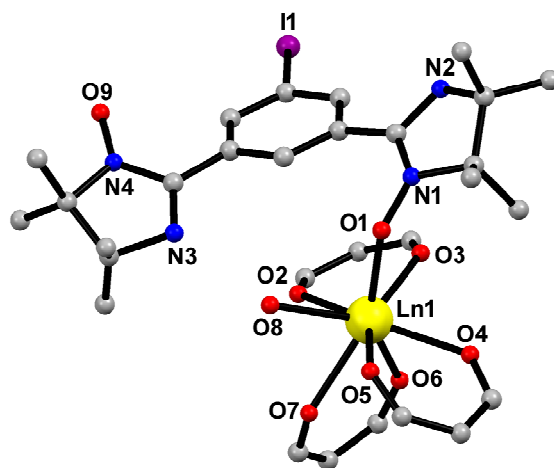


Fig. 2

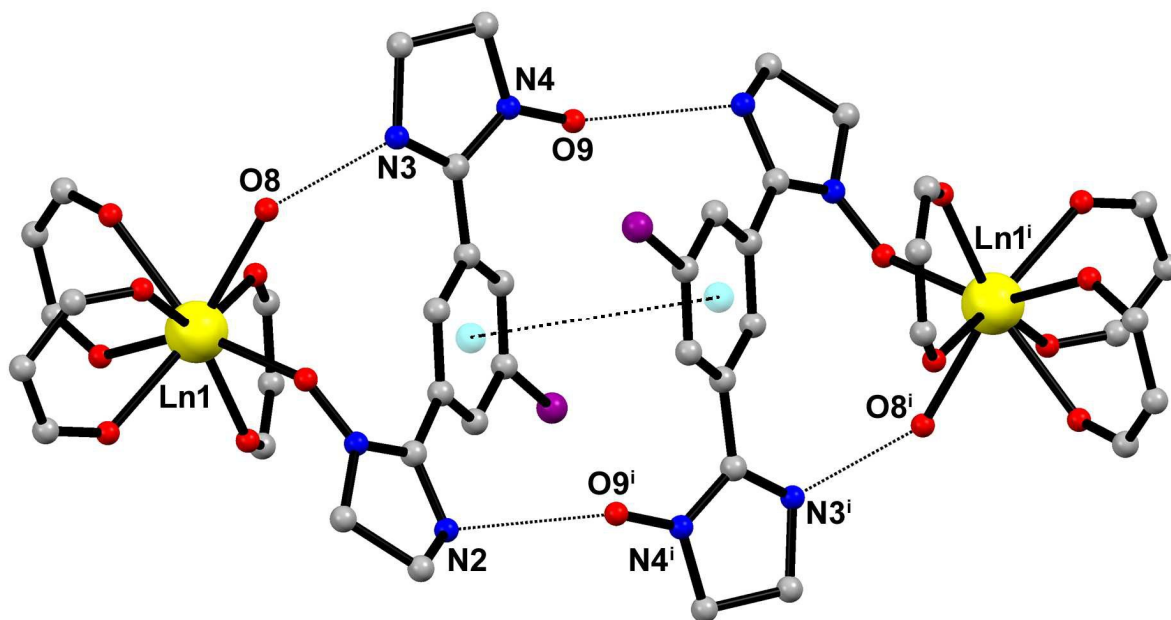


Fig. 3

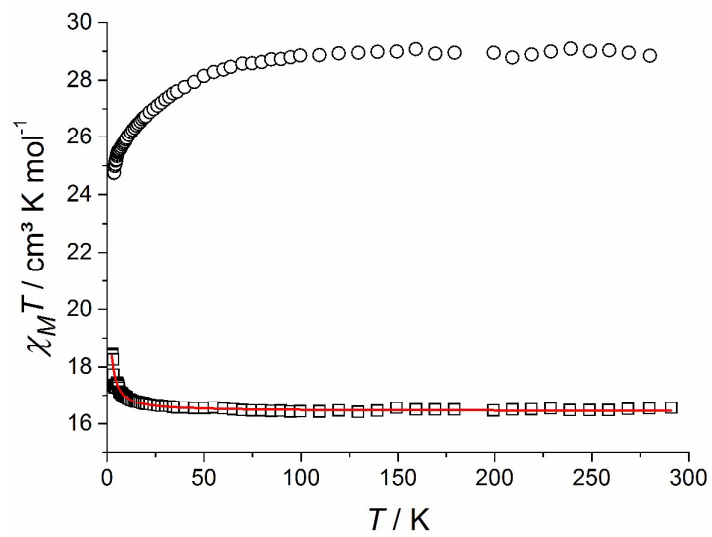


Fig. 4

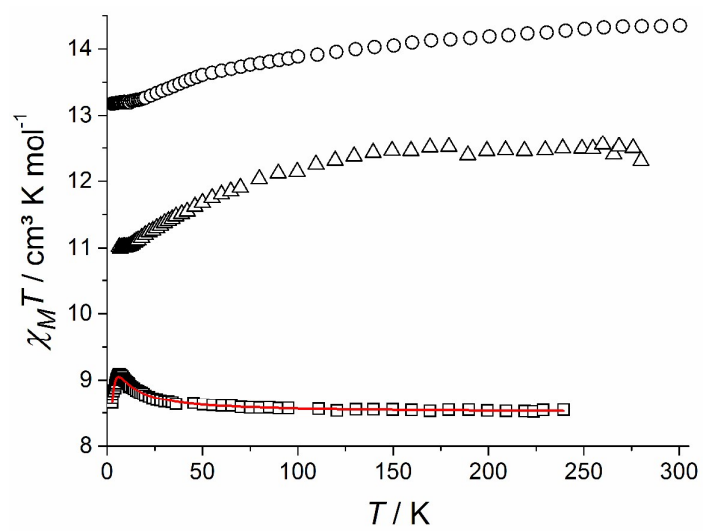


Fig. 5

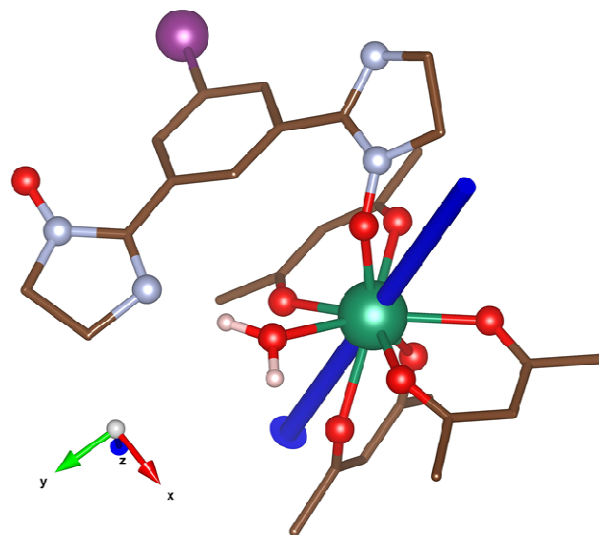


Fig. 6.

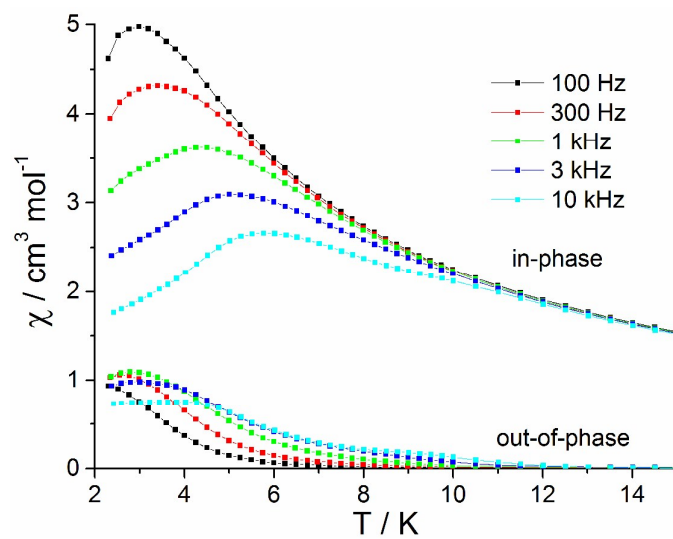


Fig. 7

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