Synthesis and Magnetic Behavior of Rare-Earth Complexes with N,O-Chelating Nitronyl Nitroxide Triazole Ligands: Example of a $[Gd^{III}\{Organic\ Radical\}_2]$ Compound with an $S = 9/2$ Ground State

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Abstract: Paramagnetic metal complexes that display a total spin ground state higher than that of the metal ion alone are interesting building blocks for the construction of molecular magnetic materials. Here we describe the synthesis and the magnetic properties of three such lanthanide complexes with two organic radicals as ligands, $[Ln(nittrz)_2(NO_3)_3]$, where Ln = Y, La, or Gd and nittrz is a nitronyl nitroxide substituted triazole derivative interacting as an η^2-N,O chelate to the metal center. For the Gd^{III} derivative a ferromagnetic exchange interaction $[J = 6.1\ cm^{-1},\ H = -J\hat{S}_{Gd}(\hat{S}_{rad1} + \hat{S}_{rad2})]$ occurs between the paramagnetic metal center ($S_{Gd} = 7/2$) and the ligands ($S_{rad1} = S_{rad2} = 1/2$) that gives rise to an $S = 9/2$ ground state. The molecular structure of this compound has been determined by X-ray diffraction.

Keywords: ferromagnetism · lanthanides · magnetic properties · nitrogen heterocycles · radicals

Introduction

In the last few years there has been growing interest in molecular coordination compounds of lanthanides due to their potential applications as luminescent probes,[1] contrast agents in magnetic resonance imaging,[2] or as building blocks in molecule-based magnetic materials.[3] In the two latter fields of potential applications, attention is more especially focused on paramagnetic complexes.

Our main interest in the field of lanthanide molecular chemistry deals with the synthesis and study of molecule-based magnetic materials obtained by association of rare-earth compounds and other paramagnetic species. We have reported several compounds comprising hetero bimetallic 4f–3d metal complexes and extended coordination polymers.[4] Recently we considered the possibility of the use of small lanthanide complexes that display a total spin higher than that of the metal ion alone as 4f building blocks. In this paper we describe a series of such compounds formed by two nitronyl nitroxide radicals interacting as N,O-chelating ligands with a lanthanide ion.

Very few compounds in which a lanthanide ion (Ln) is bound to nitronyl nitroxide radicals have been reported.[5] Most of them consist of polymeric chains formed by $Ln(hfac)_3$ moieties (hfac = hexafluoroacetylacetonate) bridged by a nitronyl nitroxide unit through the coordination of its oxygen atoms to the Ln atom. In one example the chemical interaction of the radical with the Ln atom might be considered as rather strong as it involves the intramolecular coordination of a pyridine unit giving rise to a chelating ligand.[6] Interestingly, the intramolecular Gd–radical magnetic interaction was found to be ferromagnetic in all cases. We report now on the synthesis and magnetic properties of a series of compounds consisting of a lanthanide ion (Ln = Y,[7] La, Gd) surrounded by two N,O-chelating nitronyl nitroxide radicals and three nitrato groups.

Results and Discussion

Lanthanide complexes with organic radicals as ligands are useful for the preparation of molecular materials or as contrast agents in magnetic resonance imaging (MRI) only if they are stable towards dissociation in solution. The chemical interaction of the metal with the nitronyl nitroxide moiety through the coordination of the nitroxide oxygen atom is rather weak and requires a strongly electrophilic metal

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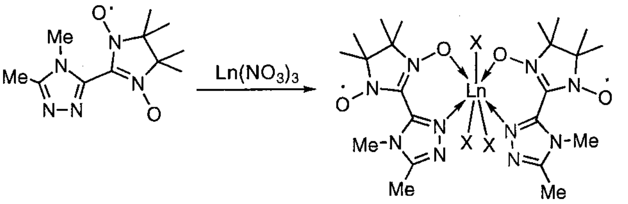
center. To overcome this limitation and to improve the stability of the Ln complexes we envisaged a derivative in which a second heteroatom can bind intramolecularly to the metal center, thus forming a chelating ligand. For this purpose we have chosen a triazole derivative substituted in the 3-position by the nitronyl nitroxide group so that both the O atom of a nitroxide and the N atom of the triazole heterocycle can coordinate to the Ln ion. The reaction of 2-(4,5-dimethyl-4*H*-1,2,4-triazol-3-yl)-4,4,5,5-tetramethyl-3-oxo-4,5-dihydro-1*H*-imidazol-1-oxyl (nittrz) with $Ln(NO_3)_3$ (Ln = Y, La, Gd) in MeOH yielded quantitatively the deep blue compounds $[Ln(nittrz)_2(NO_3)_3]$ (**1**–**3**; Ln = Y (**1**), La (**2**), and Gd (**3**), Scheme 1). These compounds were found to be very hygroscopic in the solid state and were handled in an N_2 atmosphere. They were recrystallized from MeCN solutions by slow diffusion of Et_2O.



Scheme 1. Formation of $[Ln(nittrz)_2(X_3)_3]$, X = η^2-NO_3, Ln = Y (**1**), La (**2**), and Gd (**3**).

A crystal structure analysis was performed on the Gd compound **3**. Crystals suitable for X-ray structure analysis were grown from a CH_2Cl_2/Et_2O solution. Data were collected at low temperature (263 K) because of the instability of the crystal towards the loss of solvation molecules. The unit cell contains four molecules of **3** and twelve CH_2Cl_2 solvent molecules. A view of the molecular structure is given in Figure 1 with selected bond lengths and angles in the legend.

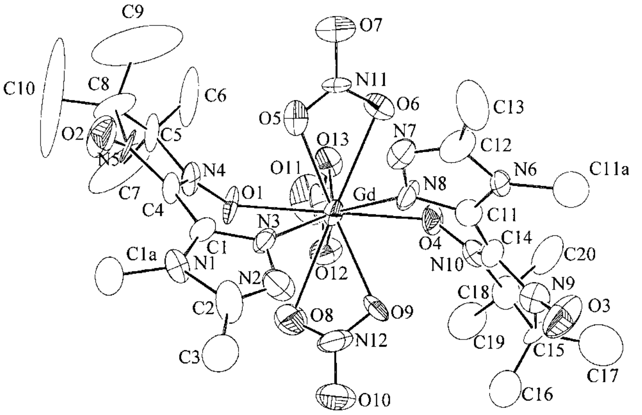


Figure 1. View of the molecular structure of $[Gd(nittrz)_2(NO_3)_3]$ (**3**). Selected bond lengths and distances (Å) and angles (°): Gd–O4: 2.430(15), Gd–O1: 2.460(15), Gd–N3: 2.556(19), Gd–N8: 2.585(17), Gd–ONO_2 (mean): 2.520; intermolecular distances: O3–O3: 5.883(39), O4–O2: 6.360(24), O2–O3: 6.338(26); angles: O1-Gd-O4: 144.9(5), N3-Gd-N8: 78.2(6), N3-Gd-O1: 70.8(5), N8-Gd-O4: 71.22(5), Gd-O1-N4: 122.2(11), Gd-O4-N10: 123.7(12), dihedral angle: O1-N4-C4-N5-O2/Gd-O1-N4: 55.90(1.48); O4-N10-C14-N9-O3/Gd-O4-N10: 52.31(1.75); nitronyl nitroxide/triazole heterocycles: 38.3(15) and 37.6(22).

The compound consists of two nitronyl nitroxide ligands forming the anticipated N,O-chelate interaction with the metal. The coordination sphere of the Gd atom is completed by the η^2-coordination of the three NO_3^- anions. It can be seen that the organic ligands adopt a head-to-head arrangement. The molecule has a C_2 symmetry axis; the Ln metal and the N atom of the nitrato group coordinated between the O atom of the radical ligands lie on this C_2 axis (Figure 1). The shortest intermolecular distance, 2.92(3) Å, was found between the O atom of a nitrato anion (O10) and the sp^2 C atom (C4) of the nitronyl nitroxide moiety of a neighboring molecule. Moreover the intermolecular distances between O3 and the centroid of the N5–O2 and N4–O1 bonds of the neighboring molecule are 6.061 and 6.604 Å, respectively. Consequently the magnetic centers in each molecule are far apart from those of the neighboring molecules. The chemical analyses as well as the unit cell parameters obtained for compounds **1** and **2** reveal that these are isostructural to the Gd complex **3** (see Table 1).

Table 1. Crystal data for compounds **1**–**3**.

	1[a]	**2**[a]	**3**[a]
	monoclinic	monoclinic	monoclinic
a (Å)	11.00(2)	10.996(4)	10.902(9)
b (Å)	15.13(2)	15.387(7)	15.138(4)
c (Å)	25.52(7)	25.630(4)	25.907(9)
β (°)	101.1(3)	100.96(2)	101.55(6)
V (Å^3)	4168(15)	4257(3)	4189(4)

[a] Crystals grown from $MeCN/Et_2O$ solutions.

Magnetic properties: The magnetic interactions between a Gd^{III} ion and either the organic nitronyl nitroxide radicals or a Cu^{II} ion were reported to be ferromagnetic. When two paramagnetic species interact with a Ln center a magnetic interaction may exist, usually antiferromagnetic, between these two species. Such superimposed ferro- and antiferromagnetic interactions have been observed in both Ln–Cu and Ln–nitronyl nitroxide compounds.[3a–c, 4a, 5] In order to evaluate the amplitude of the magnetic interaction between the organic radicals involved in this study, we investigated the magnetic behavior of compounds **1** and **2** in which the metal centers are diamagnetic.

*Diamagnetic Ln compounds **1** and **2**:* The temperature dependences of the magnetic susceptibility for compounds **1** and **2** were measured in the temperature range 2–300 K, with an applied field of 1000 Oe. The plots of $\chi_m T$ versus *T*, where χ_m is the molar magnetic susceptibility corrected for core diamagnetism and *T* the temperature, are shown in Figures 2 and 3 for compounds **1** and **2**, respectively. For both **1** and **2** at high temperature (50–300 K) $\chi_m T$ is approximately equal to $0.75\,cm^3\,K\,mol^{-1}$, the expected value for two noncorrelated $S_{rad} = 1/2$ spins. As the temperature is lowered from 50 to 2 K, $\chi_m T$ decreases very rapidly to reach $0.28\,cm^3\,K\,mol^{-1}$ for **1** and $0.03\,cm^3\,K\,mol^{-1}$ for **2** at 2 K.

The profile of these curves indicates that an antiferromagnetic interaction takes place between the organic radicals

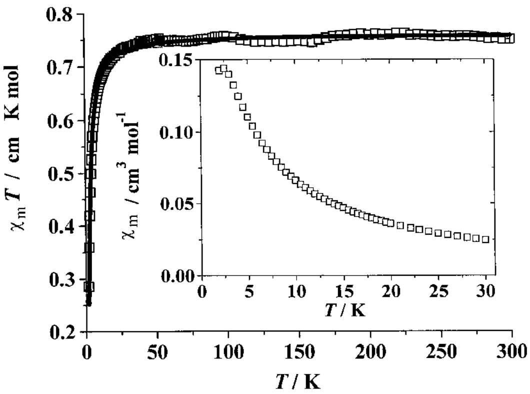


Figure 2. Experimental (□) and calculated (—) $\chi_m T$ versus T curve for compound **1**. The insert is an expanded view of χ_m versus T curve showing the maximum of χ_m at 2.5 K.

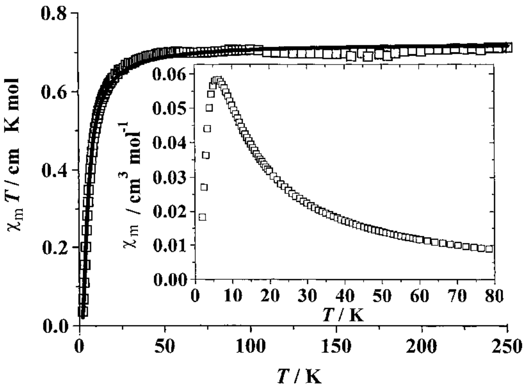


Figure 3. Experimental (□) and calculated (—) $\chi_m T$ versus T curve for compound **2**. The insert is an expanded view of χ_m versus T curve showing the maximum of χ_m at 7 K.

which tends to cancel the magnetic moment of the complex. The occurrence of this antiferromagnetic interaction is also demonstrated by the temperature dependences of the magnetic susceptibility for both **1** and **2**. The χ_m exhibits a maximum at 2.5 and 7 K, respectively (inserts, Figures 2 and 3). The X-ray structure analysis (**1**, **2**, and **3** are isostructural, vide supra) revealed that rather long intermolecular distances (>6 Å) exist between the spin carriers (i.e., the N–O moieties). It is very unlikely that an intermolecular interaction strong enough to lead to antiferromagnetic ordering at 2.5 and 7 K for **1** and **2**, respectively, takes place over such distances. Moreover, if the magnetic interactions result only from intermolecular radical–radical interactions the observed data should be the same for isostructural compounds. This is clearly not the case for **1** and **2** (see inserts, Figures 2 and 3). For these reasons the magnetic data have been analysed with a theoretical expression taking into account intramolecular magnetic interactions between the nitronyl nitroxide ligands.

The interaction parameter, J', between organic radicals was determined by least-squares fitting of the theoretical expression given in Equation (1) deduced from the spin Hamiltonian [Eq. (2)].[8] The J' values were found to be -3.1 cm^{-1} for **1** and -6.8 cm^{-1} for **2** with $g_{rad} = 2.0$. The χ^2 factors, defined in Equation (3),[9] were equal to 3.10^{-5} and 8.10^{-5} for **1** and **2**, respectively, which indicates excellent agreement between observed and calculated values. The interaction parameter J' for **1** is close to that reported for Y^{III} nitronyl nitroxide compounds.[5c]

$$\chi_m = \frac{N\beta^2}{kT}\,\frac{2g_{rad}^2}{3 + \exp\left(-\frac{J'}{kT}\right)} \qquad (1)$$

$$H = -J'\hat{S}_{rad1}\hat{S}_{rad2} \qquad (2)$$

$$\chi^2(p_1,p_2,\ldots) = \frac{1}{n^{eff} - p}\sum_i w_i[y_i - f(x_i;p_1,p_2,\ldots)]^2 \qquad (3)$$

A comparison of Figure 2 and Figure 3 as well as of the calculated interaction parameters J' shows the differences between the magnetic properties of compounds **1** and **2**. The intramolecular antiferromagnetic interaction is clearly more pronounced in **2**. The main difference between the two compounds is the nature of the diamagnetic metal center. The observation of different J' values corroborates the hypothesis that this metal center may be involved in the superexchange pathway between the two radicals.[5g] The fact that La^{III} mediates the magnetic interaction more efficiently than Y^{III} has already been observed.[4a]

The results obtained with compounds **1** and **2** confirm that an intramolecular antiferromagnetic interaction exists between the organic radical ligands. This interaction is expected to remain present when Ln is a paramagnetic ion, such as Gd^{III}. In that case the nature as well as the relative magnitude of the Gd–nittrz magnetic interaction compared to the ligand–ligand interaction will determine the spin ground state and the energy-level spectrum of the compound. It is noteworthy that in this compound the two Ln–radical interactions are expected to be the same; indeed the nitronyl nitroxide ligands are equivalent by symmetry.

*[Gd(nittrz)$_2$(NO$_3$)$_3$] (**3**)*: The variation of $\chi_m T$ *versus* T for **3** is depicted in Figure 4. At room temperature $\chi_m T$ is equal to 8.90 cm^3 K mol^{-1}, which is close to 8.62 cm^3 K mol^{-1} expected for the isolated spins $S_{Gd} = 7/2$ and two $S_{rad1} = S_{rad2} = 1/2$. $\chi_m T$ remains almost constant as T is lowered down to about 100 K, increases as T is lowered further to reach a maximum of 11.33 cm^3 K mol^{-1} at 7 K, and then decreases rapidly to about 10 cm^3 K mol^{-1} at 2 K.

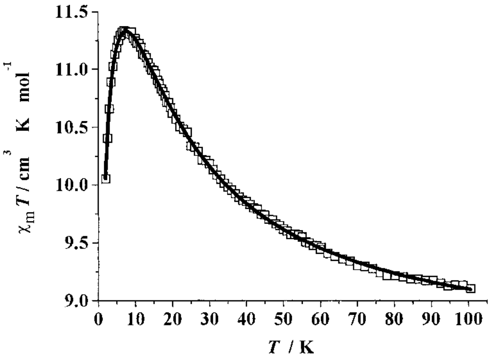


Figure 4. Experimental (□) and calculated (—) $\chi_m T$ versus T curve for compound **3**.

The profile of the curve indicates that the Gd–nitroxide radical interactions are ferromagnetic. The decrease of χ_mT below 7 K is attributed to weak intermolecular antiferromagnetic interactions. A possible saturation effect could be ruled out as the curve was not affected when recording the magnetic susceptibility of **3** at low field (5 Oe). Therefore the temperature dependence of the magnetic susceptibility was fitted with an expression of χ_m taking into account the intramolecular interaction between the Gd^{III} ion and the radicals (J), the intramolecular interaction between the two radicals (J'), and an intermolecular interaction between the molecules (J'').

Gadolinium(III) is a 4 f^7 ion with a $^8S_{7/2}$ ground state, and the first excited states are very high in energy. Consequently, the spin Hamiltonian appropriate to the system is given in Equation (4). If we take $\hat{S}' = \hat{S}_{rad1} + \hat{S}_{rad2}$ and $\hat{S} = \hat{S}' + \hat{S}_{Gd}$ then Equation (4) may be rewritten as Equation (5).

$$H = -J\hat{S}_{Gd}\hat{S}' - J'\hat{S}_{rad1}\hat{S}_{rad2} \quad (4)$$

$$H = -\frac{J}{2}(\hat{S}^2 - 2\hat{S}^2_{rad} - \hat{S}^2_{Gd}) - \frac{J'-J}{2}(\hat{S}'^2 - 2\hat{S}^2_{rad}) \quad (5)$$

The energies $E_{(S,S')}$ are given in Equations (6–9) and the $g_{(S,S')}$ Zeeman factors associated with these levels are given in Equations (10–13). The molecular susceptibility is given in Equation (14) and F is defined in Equation (15).

$$E_{(\frac{9}{2},1)} = 0 \quad (6)$$

$$E_{(\frac{7}{2},1)} = \frac{9}{2}J \quad (7)$$

$$E_{(\frac{5}{2},1)} = 8J \quad (8)$$

$$E_{(\frac{7}{2},0)} = \frac{7}{2}J + J' \quad (9)$$

$$g_{(\frac{9}{2},1)} = \frac{22}{99}g_{rad} + \frac{77}{99}g_{Gd} \quad (10)$$

$$g_{(\frac{7}{2},1)} = \frac{4}{63}g_{rad} + \frac{59}{63}g_{Gd} \quad (11)$$

$$g_{(\frac{5}{2},1)} = -\frac{10}{35}g_{rad} + \frac{45}{35}g_{Gd} \quad (12)$$

$$g_{(\frac{7}{2},0)} = g_{Gd} \quad (13)$$

$$\chi_m = \frac{N\beta^2F}{kT - J''F} \quad (14)$$

$$F = \frac{\frac{495}{2}g^2_{(\frac{9}{2},1)} + 126g^2_{(\frac{7}{2},0)}\exp\left(-\frac{7J+2J'}{2kT}\right) + 126g^2_{(\frac{7}{2},1)}\exp\left(-\frac{9J}{2kT}\right) + \frac{105}{2}g^2_{(\frac{7}{2},0)}\exp\left(-\frac{8J}{kT}\right)}{10 + 8\exp\left(-\frac{7J+2J'}{2kT}\right) + 8\exp\left(-\frac{9J}{2kT}\right) + 6\exp\left(-\frac{8J}{kT}\right)} \quad (15)$$

Least-squares fitting of the experimental data leads to $J = 6.1$ cm^{-1}, $J' = -7.0$ cm^{-1} and $J'' = -0.009$ cm^{-1} with $\chi^2 = 2.5 \times 10^{-4}$,[9] which indicates an excellent agreement between observed and calculated values (g_{Gd} and g_{rad} were taken equal to 2.00).

The interaction parameter between the nitronyl nitroxides, J', has the same value in **3** as in **2**. This behavior can be understood assuming that the 4 f orbitals of Gd^{III} and La^{III} have much the same diffuseness. Consequently the Ln–nitroxide overlap integrals should be the same for both **2** and **3**.[10] The intermolecular interaction, J'', is very weakly antiferromagnetic. The Gd–radical interaction, J, is ferromagnetic as already observed in such compounds. However the magnitude of this ferromagnetic interaction is much more pronounced than for related Gd–nitronyl nitroxide interactions.[5a, d, e] It is noticeable that a Gd–nitronyl nitroxide interaction of the same magnitude as in **3** was found in a compound in which the organic radical is also chelating.[6] The chelating coordination increases the magnetic interaction most probably by imposing specific angles for the Ln-O-N bond as well as between the imidazolyl group and the plane defined by Ln-O-N. If one compares the Ln-O-N angles of the reported compounds, they are smaller for the chelated than for the nonchelating compounds (122–126°compared with 140–180°). This might lead to a better overlap between the singly occupied π^* orbital of the nitroxide and the 5d and/or 6s orbitals of the metal.[11] Indeed, the ferromagnetic interaction between the lanthanide ion and paramagnetic ligands is proposed to involve the empty 5d and 6s orbitals of the metal, a fraction of the unpaired electrons of the organic ligands being transferred into these empty orbitals. According to Hund's rule, the 4 f electrons are expected to be aligned parallel to these 5d and 6s electrons, thus leading to ferromagnetism.[4d, 5g, 12]

A diagram of the low-lying energy levels, $E_{(S,S')}$, with the calculated interaction parameters is shown in Figure 5. It appears that the ground state of **3** is $S = 9/2$, that is, the three spins within the molecule are aligned in the same direction. The energy gap between the ground nonet and the first excited septet was found to be equal to 14 cm^{-1}, the second excited septet state being located at 28 cm^{-1}. The field dependence of the magnetization of compound **3** was measured at 2 K. The M versus H curve is shown in Figure 6. In this figure the experimental magnetization is compared to the theoretical magnetization given by the Brillouin function for an $S = 9/2$ total spin and to the sum of isolated Gd^{III} and nitronyl nitroxides ($S_{Gd} = 7/2 + 2 \times S_{rad} = 1/2$). For any value of the field the experimental magnetization is larger than that of the noncorrelated spin system but very close to the value expected for an $S = 9/2$ state. This comparison definitely confirms that **3** has an $S = 9/2$ ground state.

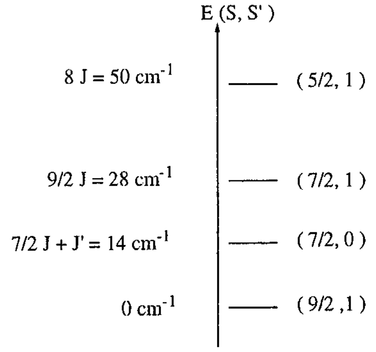


Figure 5. Energy levels $E_{(S,S')}$ of **3**.

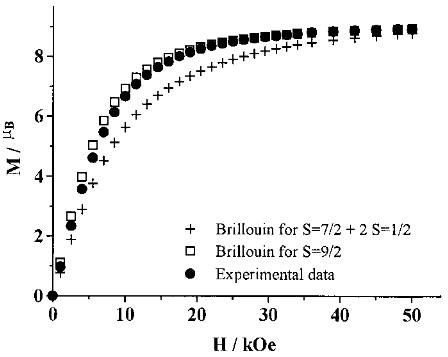


Figure 6. Field dependence (H/kOe) of the magnetization (M/μ_B) of compound **3** at 2 K (●). Theoretical magnetization calculated for isolated $S = 7/2 + 2 \times S = 1/2$ (+) and for $S = 9/2$ (□).

Conclusion

The formation of lanthanide nitronyl nitroxide complexes in which the organic radical acts as a chelating ligand leads to rather stable Ln-radical coordination without the need of strongly electron-withdrawing groups. Moreover, as observed in $[Gd(nittrz)_2(NO_3)_3]$ (**3**), the chelate reinforces the ferromagnetic interaction between the metal and the two radicals present in the coordination sphere leading to a compound with an $S = 9/2$ ground state. In the field of molecular magnetism such compounds with high total spin are interesting candidates for the construction of extended networks by molecular assembly strategies. It can be emphasized that because of the rather weak Ln–radical magnetic interactions compared to related transition metal–radical compounds a long-range magnetic ordering can only occur at low temperature. Moreover, contrary to what is usually observed within the Ln-ion series we obtained the same molecular structure for the three lanthanides involved in our study. If this trend was confirmed for the whole series of Ln^{III} ions, this would allow an accurate investigation of the Ln–nitroxide magnetic interactions.

Experimental Section

General methods: All reactions were performed with standard Schlenk tube and vacuum line techniques. The solvents used were dried (MeCN over P_2O_5, Et_2O over Na, and MeOH over Mg) and distilled under N_2 prior to use. The nitronyl nitroxide derivative[13] and $Ln(NO_3)_3 \cdot x H_2O$[1a] were prepared as described in the literature.

Crystallographic data collection and structure determination: For compound **3**, X-ray data collection was accomplished at 263(2) K with a needle crystal protected by nujol. Accurate cell dimensions were obtained from 25 reflections with $11.790 \geq \theta \geq 4.535°$. Crystal data, $C_{25}H_{42}GdCl_6N_{13}O_{13}$; $M = 1102.7$; space group: monoclinic, $P2_1/n$ (no. 14); $a = 11.135(3)$, $b = 15.156(7)$, $c = 26.490(7)$ Å, $\beta = 100.502(12)°$, $V = 4395.5(25)$ Å^3; $Z = 4$; $\rho_{calc} = 1.666$ g cm^{-3}; $2\theta_{max} = 49.90°$; scan mode $\theta - 2\theta$; F(000) = 2212; 8097 reflections measured; 7672 independent reflections; 2672 reflections were observed with $F^2 > 2\sigma(F^2)$. A decay correction (−9.4%) was performed; absorption correction: semiempirical ψ-scan method, $T_{min} = 0.8337$; $T_{max} = 0.9974$, $\mu(Mo_{K\alpha}) = 1.944$ mm^{-1}; structure solution: direct methods with SHELXS-86,[14] structure refinement: least-squares against F_o^2 with SHELXL-93;[15] 508 parameters; hydrogen atoms were included as fixed contributors in idealized positions; refinement of variables with anisotropic thermal parameters (except N9, C11 and C11a) gave $R = 0.0954$ and $wR = 0.1838$ and the residual electron density 1.137 (0.97 from Gd) and −1.507 (0.02 from Gd). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100728. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Compounds **1**, **2**, and **3** were prepared by the same procedure.

$[Gd(nittrz)_2(NO_3)_3]$ (**3**): A solution of $Gd(NO_3)_3 \cdot x H_2O$ (450 mg, ca. 1 mmol) and the nitronyl nitroxide (756 mg, 3 mmol) in MeOH (15 mL) was stirred at room temperature for 5 h. The solvent was then removed in vacuo, the residue was redissolved in CH_2Cl_2, and Et_2O was added. The precipitate was collected by filtration, washed with Et_2O, and dried to yield **3** (0.8 g) as a deep blue solid. A crystalline solid was obtained by diffusion of Et_2O into a MeCN solution of **3**.

Compound 1: IR (KBr): $\tilde{\nu} = 2996$ (w), 1503 (s), 1375 (s), 1304 (s), 1178 (m), 1139 (w)1034 cm^{-1} (w); $C_{22}H_{36}N_{13}O_{13}Y \cdot 2\,MeCN$ (861.61): calcd C 36.24, H 4.91, N 24.38, Y 10.32; found C 36.81, H 4.93, N 24.56, Y 10.39.

Compound 2: IR (KBr): $\tilde{\nu} = 2989$ (w), 1636 (w), 1454 (s), 1381 (s), 1310 (s), 1178 (m), 1139 (w), 1035 cm^{-1} (w); $C_{22}H_{36}N_{13}O_{13}La \cdot 2\,MeCN$ (911.61): calcd C 34.25, H 4.64, N 23.04, La 15.24; found C 34.26, H 4.78, N 22.46, La 15.20.

Compound 3: UV/Vis (MeOH): λ_{max} (ε) = 201 (28000), 243 (13770), 339 (28200), 561 nm (750); IR (KBr): $\tilde{\nu} = 2997$ (w), 1636 (m), 1507 (m), 1458 (m), 1384 (s), 1307 (m), 1176 (m), 1137 cm^{-1} (w); $C_{22}H_{36}N_{13}O_{13}Gd \cdot 2\,MeCN$ (929.96): calcd C 33.58, H 4.55, N 22.59; found C 33.45, H 4.68, N 22.54.

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