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Systematic Investigation of the Nature of The Coupling between a Ln(III) Ion (Ln = Ce(III) to Dy(III)) and Its Aminoxyl Radical Ligands. Structural and Magnetic Characteristics of a Series of {Ln(organic radical)$_2$} Compounds and the Related {Ln(Nitrone)$_2$} Derivatives

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Abstract: Numerous molecular compounds in which a paramagnetic Ln(III) ion is in interaction with a second spin carrier such as a transition metal ion or an organic radical have been described. However, except for the isotropic Gd(III) ion, very little is known concerning the nature (*ferro-* or *antiferromagnetic*) and mechanism of the interaction involving a Ln(III) ion. This study addresses the problem of the interaction between the Ln(III) ions displaying spin−orbit coupling and an organic radical. The magnetic properties of a series of isostructural compounds, {Ln(organic radical)$_2$(NO$_3$)$_3$}, comprising a Ln(III) ion (Ln = Ce to Dy) surrounded by two N,O-chelating aminoxyl radicals (3-nitronyl nitroxide-4,5-dimethyltriazole) have been investigated. The experimental approach used to get insight into the {Ln-Radical} coupling occurring within these compounds is based on the knowledge of the intrinsic paramagnetic contribution of the metal ion. This contribution has been deduced from the corresponding {Ln(Nitrone)$_2$(NO$_3$)$_3$} derivatives (Nitrone stands for 3-*N*-*tert*-butylnitrone-4,5-dimethyltriazole), where the Ln(III) ion is now in a diamagnetic surrounding. A simple mathematical difference of the magnetic susceptibilities of {Ln(organic radical)$_2$(NO$_3$)$_3$} and the corresponding {Ln(Nitrone)$_2$(NO$_3$)$_3$} derivatives then permitted the nature of the correlations within the {Ln(organic radical)$_2$(NO$_3$)$_3$} compounds to be established. Moreover, these results have been confirmed by the field dependence of the magnetization for each derivative. A systematic investigation of the isostructural series of compounds allowed the evolution of these interactions to be compared as a function of the electronic configuration of the 4f orbitals. For the Ln(III) with 4f^1 to 4f^5 electronic configurations the {Ln-organic radical} interaction is antiferromagnetic. Conversely, this interaction was found to be ferromagnetic for the configurations 4f^7 to 4f.^{10} These interactions have been clearly indicated for each Ln(III).

Introduction

Molecular coordination compounds of lanthanide ions attract a growing interest in material science due to their luminescence[1,2] or magnetic properties.[3−15] The rather large and anisotropic magnetic moments of most of the lanthanide(III) ions, Ln(III), make these ions appealing building blocks in the molecular approach of magnetic materials. Numerous compounds containing a Ln(III) ion and paramagnetic species such as a transition metal ion[3−10] or an organic radical[11−15] have been described. However, except for the isotropic Gd(III), which has an $^8S_{7/2}$ single-ion ground state, very little is known concerning

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the nature and magnitude of the coupling in such compounds nor the evolution of the magnetic properties along the lanthanide series. One of the reasons for this situation is the orbital contribution occurring for most of the Ln ions, i.e., the ligand field effect on the magnetic characteristics of the ions displaying spin−orbit coupling. For such a Ln(III) ion the $4f^n$ configuration is split into $^{2S+1}L_J$ spectroscopic levels by interelectronic repulsion and spin−orbit coupling. Each of these states is further split in Stark sublevels by the crystal field perturbation. The number of Stark sublevels depends on the site symmetry of the Ln ion.[16] For C_1 symmetry, which is often the case in molecular compounds, $2J + 1$ sublevels are expected when the number of 4f electrons is even and $J + {}^1/_2$ when it is odd. At room temperature, all Stark sublevels of the $^{2S+1}L_J$ ground state, or those of the low-lying first excited states for Sm(III) and Eu(III), are thermally populated. As the temperature is lowered, a depopulation of these sublevels occurs and consequently $\chi_{\mathrm{Ln}}T$, where χ_{Ln} is the magnetic susceptibility of the Ln(III) ion, decreases. The temperature dependence of χ_{Ln} deviates with respect to the Curie law. When the Ln(III) ion interacts with another paramagnetic species, the temperature dependence of $\chi_{\mathrm{M}}^{\mathrm{Ln}}T$ for the compound ($\chi_{\mathrm{M}}^{\mathrm{Ln}}$ stands for the molar magnetic susceptibility) is due to both the variation of $\chi_{\mathrm{Ln}}T$ and the coupling between the Ln(III) ion and the second spin carrier. Consequently, information about the nature of the interactions between a Ln(III) ion with a first-order orbital momentum and the second spin carrier cannot be unambiguously deduced only from the shape of the $\chi_{\mathrm{M}}^{\mathrm{Ln}}T$ versus T curve. Moreover, the theoretical analysis of the magnetic data of such a compound is impeded by the lack of a general theoretical model to describe the χ_{Ln} behavior of a Ln(III) ion in its ligand field.

Recently, we described a compound, {Ln(organic radical)$_2$(NO$_3$)$_3$}, consisting of a Ln(III) ion, La(III) or Gd(III), surrounded by two N,O-chelating paramagnetic ligands, i.e., nitronyl nitroxide radicals.[17] These complexes, in which the organic radical acts as a chelating ligand, led to rather stable Ln-radical coordination without the need of strongly electron withdrawing anions. Moreover, as observed for the Gd(III) derivative, the chelate reinforces the coupling between the metal and the two radicals present in the coordination sphere leading to an $S = {}^9/_2$ ground state for the Gd(III) compound. In the field of molecular magnetism such high-spin compounds are interesting candidates for the construction of extended networks by molecular assembling strategies. Interestingly, we obtained the same molecular structure for both the La(III) and the Gd(III) compounds. This prompted us to extend the study to the other lanthanide ions to gain some information concerning the Ln-aminoxyl interaction.

We now report that the isostructurality remains valid along the lanthanide series. This allowed us to compare the magnetic behavior of these compounds excluding any change in the magnetic properties due to differences of the molecular structures. Moreover, the problem of the spin−orbit coupling of the Ln(III) ions has been overcome by an experimental approach involving {Ln(nitrone)$_2$(NO$_3$)$_3$} compounds. In the latter, the coordination sphere of the Ln(III) ion is the same as that for the {Ln(organic radical)$_2$(NO$_3$)$_3$} compounds but with the Ln ion in a diamagnetic surrounding. A comparison of the magnetic characteristics of the Ln(organic radical) with those of the corresponding Ln(Nitrone) compound led to accurate information on the ferro- or antiferromagnetic nature of the {Ln(III)−aminoxyl radical} interaction. A first result of this approach showed the {Ho−aminoxyl} interaction to be ferromagnetic.[18] In this report we provide insight into the {Ln(III)−organic radical} interaction including the lanthanide ions with a first-order orbital momentum from Ce(III) to Dy(III).

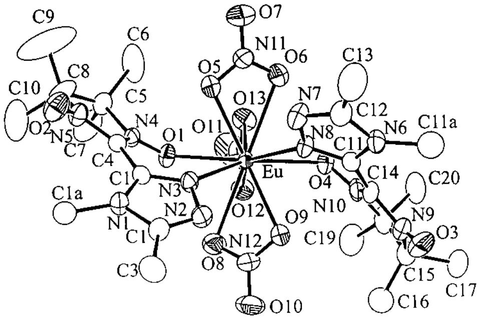
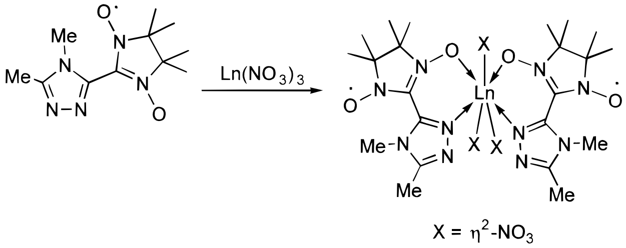


Figure 1. Molecular structure (ORTEP, 20% ellipsoids) and numbering scheme for {Eu(NitTRZ)$_2$(NO$_3$)$_3$}. Selected bond lengths (Å) and angles (deg): Eu−O1 2.419(4); Eu−O4 2.440(4); Eu−N3 2.552(5); Eu−N8 2.595(5); Eu−ONO$_2$ 2.462(5) to 2.607(5); O1−N4 1.278(6); N5−O2 1.264(6); N4−C4 1.324(7); C4−N5 1.354(8). Intermolecular distances: O3···O3^{i} 4.655(11); O3···N9^{ii} 5.280(8); O2···O4^{iii} 6.080(7); O4···N5^{vi} 5.672(7). Angles: O1−Eu−O4 144.5(1); N4−O1−Eu 126.5(3); N3−Eu−O1 70.9(2); N10−O4−Eu 122.3(3); N8−Eu−O4 69.4(2). Dihedral angles: Eu−O1−N4−C4 47.3(7); Eu−O4−N10−C14 55.4(7). (Symmetries used: (*i*) $1 - x, -1 - y, -z$; (*ii*) $1 - x, -1 - y, -z$; (*iii*) $1.5 - x, 0.5 + y, 0.5 - z$; (*iv*) $1.5 - x, 0.5 + y, 0.5 - z$.)

Scheme 1. Formation of {Ln(NitTRZ)$_2$(NO$_3$)$_3$}, Ln = Ce, Pr, Nd, Sm, Eu, Tb, Dy



Results

{Ln(organic radical)$_2$(NO$_3$)$_3$} Compounds. The compounds involved in this study were synthesized by the reaction of the nitronyl nitroxide substituted triazole, 2-(4′,5′-dimethyl-1′,2′,3′-triazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide, NitTRZ, with Ln(NO$_3$)$_3$·xH$_2$O salts (Ln = Ce(III) to Lu(III) except the radioactive Pm) in MeOH as previously described for Gd(III) (Scheme 1). The deep blue {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds are very hygroscopic in the solid state and were handled in a N$_2$ atmosphere. A recrystallization from MeCN by slow diffusion of Et$_2$O led to single crystals of {Ln(NitTRZ)$_2$(NO$_3$)$_3$} for Ln = Ce to Dy. Only the crystallized complexes were considered for the subsequent study.

An X-ray crystal structure analysis was performed on the Eu(III) compound. The unit cell contains four molecules of the complex and twelve MeCN solvent molecules. A view of the molecular structure is given in Figure 1 with selected distances and angles; additional crystal data can be found in Table 1. The molecular structure consists of two nitronyl nitroxide ligands interacting as N,O-chelates with the metal center. The coordination sphere of the Eu(III) ion is completed by the η^2-coordination of the three NO$_3^-$ anions. The molecular structure of this

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Table 1. Crystal Data and Structure Refinement for {Eu(NitTRZ)$_2$(NO$_3$)$_3$} and {Pr(Nitrone)$_2$(NO$_3$)$_3$}

	{Eu(NitTRZ)$_2$(NO$_3$)$_3$}, 3MeCN	{Pr(Nitrone)$_2$(NO$_3$)$_3$}
empirical formula	$C_{28}H_{45}EuN_{16}O_{13}$	$C_{36}H_{64}N_{22}O_{22}Pr_2$
formula weight	965.76	1438.91
a (Å)	10.929(3)	10.199(2)
b (Å)	15.212(7)	10.630(2)
c (Å)	25.523(9)	14.062(2)
α (deg)	90	82.49(1)
β (deg)	101.03(1)	69.36(1)
γ (deg)	90	83.35(1)
V (Å^3)	4165(3)	1410.6(4)
Z	4	1
space group	$P2_1/n$	$P1$
T (K)	263	293
λ (Å)	0.71073	0.71069
ρ_{calcd} (g·cm^{-3})	1.540	1.694
μ (mm^{-1})	1.583	1.801
θ_{max} (deg)	26	25
no. of reflcns used [$I > 2\sigma(I)$]^a	6183	3724
no. of parameters refined	523	735
R_1	0.040	0.030
wR_2 [$I > 2\sigma(I)$]^b	0.105	0.073
GoF	1.04	1.01

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

compound is almost superimposable with that of the corresponding {Gd(NitTRZ)$_2$(NO$_3$)$_3$} previously reported,[17] except for the solvent molecules. The shortest intermolecular distance, 2.880(8) Å, is found between an O atom (O10) of a nitrato anion and the sp^2 C atom (C4) of a nitronyl nitroxide unit of a neighboring molecule. The shortest intermolecular distances involving the O atoms of the nitronyl nitroxide groups are found for C13 with O2 (3.283(9) Å) and C10 with O3 (3.589(11) Å), respectively. Moreover, the shortest separation involving two NO units is 4.655(11) Å, between O3 and O3* ($1 - x$, $-1 - y$, $-z$). Consequently, the magnetic centers of each molecule can be considered apart enough from those of the neighboring molecules to prevent substantial intermolecular magnetic interactions.

The isostructurality of the series of compounds was established by means of their cell parameters (Table 2). All compounds display very similar cell parameters. These data are consistent with the occurrence of the same molecular topology and solvent molecules within the lattice. Only a small shrinking from {La(NitTRZ)$_2$(NO$_3$)$_3$} to {Dy(NitTRZ)$_2$(NO$_3$)$_3$} was found as expected owing to the decrease of the ionic radii of the Ln(III) ions from the left to the right of the series.

Magnetic Behaviors. The magnetic behavior of {Gd(NitTRZ)$_2$(NO$_3$)$_3$} was found to be driven by the substantial ferromagnetic interaction between the Gd(III) and its paramagnetic ligands, the interactions with the neighboring complexes being negligibly small.[17] Consequently, the magnetic behavior along the isostructural series reported in this paper should mainly arise from the molecular unit. The temperature dependence of the molar magnetic susceptibility, χ_M^{Ln}, for each of the {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds, Ln = Ce, Pr, Nd, Sm, Eu, Tb, and Dy, was measured on a polycrystalline sample in the temperature range 2−300 K, with an applied field of 1000 Oe. Subsequently, a chemical analysis was performed on each sample to determine its exact composition (remaining MeCN solvate molecules).

(a) Tb (4f^8) and Dy (4f^9) Compounds. The temperature dependence of the magnetic susceptibility of {Tb(NitTRZ)$_2$(NO$_3$)$_3$} is shown as a $\chi_M^{Tb}T$ versus T plot in Figure 2. At 300 K, $\chi_M^{Tb}T$ is equal to 13.12 cm^3 K mol^{-1}, close to the value calculated for the uncorrelated magnetic moments of the two $S = {}^1/_2$ radicals and a Tb(III) ion. As the temperature is lowered, $\chi_M^{Tb}T$ increases more and more rapidly to reach a maximum of 14.67 cm^3 K mol^{-1} at 8 K and then decreases to reach 12.53 cm^3 K mol^{-1} at 2 K. The profile of the curve is very similar to what was observed previously for the corresponding Gd(III) complex. The increase of $\chi_M^{Tb}T$ as the temperature is lowered is characteristic of an enlargement of the total magnetic moment of the molecule as a result of ferromagnetic interaction between the spin carriers. The decrease observed below 8 K can be attributed to weak intermolecular antiferromagnetic interactions between neighboring molecules, as observed for the Gd(III) compound too.

The $\chi_M^{Dy}T$ versus T curve of {Dy(NitTRZ)$_2$(NO$_3$)$_3$} is similar to that of the Tb compound (Figure 2). At 300 K, $\chi_M^{Dy}T$ is equal to 14.18 cm^3 K mol^{-1} and remains almost constant as the temperature is lowered to 50 K. Below this temperature $\chi_M^{Dy}T$ increases rapidly to reach 15 cm^3 K mol^{-1} at 10 K before dropping to 11.15 cm^3 K mol^{-1} at 2 K. As for {Tb(NitTRZ)$_2$(NO$_3$)$_3$}, this behavior is consistent with ferromagnetic interactions within the complex.

(b) Ce (4f^1) to Eu (4f^6) Compounds. As a general trend, for the complexes of the paramagnetic Ln(III) ions of the first half of the series the $\chi_M^{Ln}T$ versus T curves are characterized by a continuous decrease as the temperature is lowered (Figure S1, Supporting Information). At 300 K, the experimental $\chi_M^{Ln}T$ values are close to the values expected for the noncorrelated magnetic moments of the radicals and the corresponding Ln(III) ion. The values observed for each compound at 300 and 2 K are given in Table 2. The magnetic behavior of the Sm(III) and Eu(III) compounds is somewhat peculiar. For these ions the first excited state is sufficiently low in energy to be thermally populated, even below 300 K. Consequently, for these two compounds the increase of $\chi_M^{Ln}T$ above 100 K is more pronounced than that for the other {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds. Note that the ground state of Eu(III) is nonmagnetic. Consequently, the low-temperature magnetic behavior for {Eu(NitTRZ)$_2$(NO$_3$)$_3$} is governed by the interaction between the two paramagnetic ligands (Figure 3). The rapid decrease of $\chi_M^{Eu}T$ below 20 K can be attributed to antiferromagnetic interactions between the nitronyl nitroxide units. The occurrence of this antiferromagnetic interaction is also demonstrated by the maximum exhibited by χ_M^{Eu} at 3 K (insert, Figure 3). In the particular case of the Eu compound, the magnetic behavior has been analyzed by a theoretical model (see below).

For the Ce(III) to Sm(III) compounds of this series, the profile of the $\chi_M^{Ln}T$ versus T curves does not allow the nature of the interaction between the Ln(III) ion and its paramagnetic ligands to be determined. As described above, the temperature dependence of χ_{Ln} for a Ln(III) with a first-order angular momentum deviates with respect to the Curie law. Consequently, the temperature dependence of $\chi_M^{Ln}T$ obtained for these {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds is the result of the superimposition of both the variation of the intrinsic susceptibility, χ_{Ln}, of the Ln(III) ion and the {Ln−radical} interaction. And even in the case of a continued decrease of $\chi_M^{Ln}T$ as observed for these compounds, the {Ln−radical} interaction could be either ferro- or antiferromagnetic. Indeed, if the decrease due to χ_{Ln} is larger than the increase resulting from ferromagnetic {Ln−radical} interactions a continuous decrease of $\chi_M^{Ln}T$ will be observed as the temperature is lowered.[18] The same overall behavior will also result from antiferromagnetic {Ln−radical} interactions

Table 2. Cell Parameters and High- (300 K) and Low-temperature (2 K) Values of $\chi_M^{Ln}T$ for {Ln(NitTRZ)$_2$(NO$_3$)$_3$}, Ln = La to Dy

	La[a]	Ce	Pr	Nd	Sm	Eu	Gd[a]	Tb	Dy
a (Å)	10.996(4)	10.996(9)	10.983(3)	10.995(3)	10.925(65)	10.929(3)	10.902(9)	10.851(7)	10.875(8)
b (Å)	15.387(7)	15.356(5)	15.296(6)	15.301(5)	15.236(5)	15.212(7)	15.138(4)	15.126(7)	15.186(5)
c (Å)	25.630(4)	25.63(2)	25.597(13)	25.639(9)	25.640(135)	25.523(9)	25.907(9)	25.851(8)	25.782(8)
β (°)	100.96(2)	100.87(6)	100.95(3)	101.03(1)	101.6(3)	101.03(1)	101.55(6)	101.36(6)	101.4(1)
V (Å^3)	4257(3)	4250(5)	4222(3)	4233	4183	4165(3)	4189(4)	4160(3)	4174(4)
$\chi T_{300\,K}$[b]	0.75	1.27	2.14	2.10	0.83	1.93	8.90	13.12	14.18
$\chi T_{2\,K}$[b]	0.03	0.28	0.59	0.41	0.29	0.24	10.0	12.53	11.15

[a] Taken from ref 17. [b] In cm^3 K mol^{-1}.

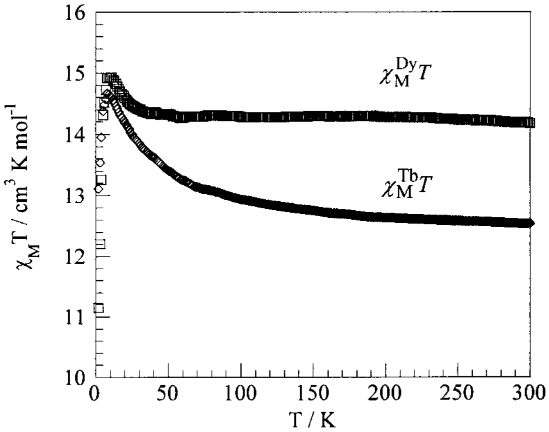


Figure 2. Experimental $\chi_M^{Ln}T$ versus T curves for {Ln(NitTRZ)$_2$(NO$_3$)$_3$}, Ln = Tb, Dy.

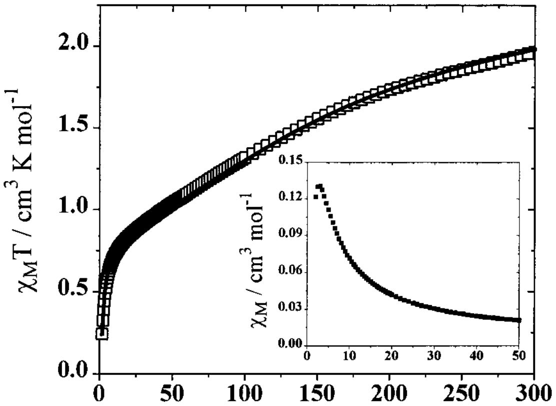
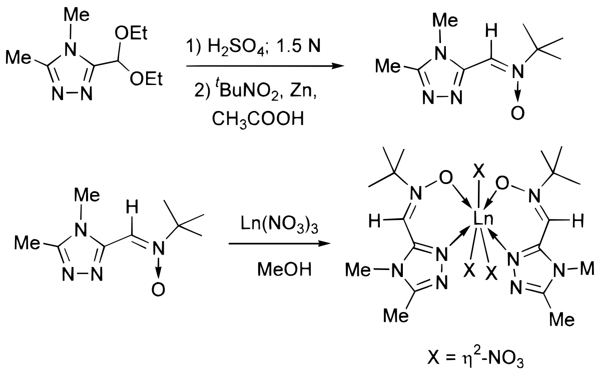


Figure 3. Experimental and calculated (—) $\chi_M^{Eu}T$ versus T curve for {Eu(NitTRZ)$_2$(NO$_3$)$_3$}. The insert is an expanded view of the experimental χ_M^{Eu} versus T curve showing the maximum of χ_M^{Eu}.

superimposed on the decrease of $\chi_{Ln}T$. Consequently, information about the nature of the magnetic interactions between these Ln(III) ions and the aminoxyl ligands cannot be unambiguously deduced only from the feature of the $\chi_M^{Ln}T$ versus T curves.

To gain some information concerning the interaction between Ln(III) ions displaying spin−orbit coupling and the aminoxyl ligands, we decided to address the problem via an experimental approach. One way of making the interaction apparent would be to subtract from $\chi_M^{Ln}T$ the contribution arising from the thermal depopulation of the Stark sublevels of Ln(III), $\chi_{Ln}T$. The temperature dependence of $\chi_{Ln}T$ is directly related to the local contribution of the ligand field onto the Ln(III) ion and thus can be obtained from an isostructural Ln(III) complex with a diamagnetic surrounding. This approach has been applied already to the investigation of the {Ln(III)−Cu(II)} interactions in both bimetallic and polymeric coordination compounds containing a Ln(III) and the transition metal ions. Through the replacement of the paramagnetic Cu(II) by a diamagnetic ion, the corresponding $\chi_{Ln}T$ contribution could be obtained.[19,20] In the present case, the problem is somewhat more tricky. To allow a comparison between $\chi_M^{Ln}T$ and $\chi_{Ln}T$, the ligand field in the compound used to determine $\chi_{Ln}T$ has to be the same as that for the {Ln(organic radical)$_2$(NO$_3$)$_3$} series. A diamagnetic equivalent of the nitronyl nitroxide radical has to be found. The molecule chosen as a diamagnetic counterpart to the nitronyl nitroxide radical was the N-*tert*-butylnitrone-substituted triazole derivative, hereafter called Nitrone. Both the nitrone and the nitronyl nitroxide-substituted triazole are very much the same as far as the moieties which are involved in the coordination to a metal center are concerned, i.e., the nitrogen heterocycle and the *N*-oxide fragment. Moreover, the coordination behavior of nitrones to a metal center has been shown to be very similar to that of nitronyl nitroxides.[21]

Scheme 2



{Ln(Nitrone)$_2$(NO$_3$)$_3$} Compounds. The nitrone has been prepared as described in Scheme 2. The {Ln(Nitrone)$_2$(NO$_3$)$_3$} compounds were synthesized by reaction of the nitrone derivative with the Ln(NO$_3$)$_3$ salts, in a 2:1 ratio, in MeOH. A crystallization from a MeCN−MeOH solution by slow diffusion of Et$_2$O led to microcrystalline {Ln(Nitrone)$_2$(NO$_3$)$_3$} for Ln = Ce(III) to Dy(III). These compounds are colorless or slightly colored depending on the Ln(III) ion except for the Ce derivative which is orange.

An X-ray crystal structure analysis was performed on the Pr(III) compound. Two molecules corresponding to two optical isomers form the asymmetric unit. A view of the molecular structure is given in Figure 4, and crystallographic data are presented in Table 1. The compound consists of two nitrone ligands interacting as N,O-chelates with the metal center. The coordination sphere of the Pr(III) ion is completed by the η^2-coordination of three NO$_3^-$ anions. The bond length and angles of the coordination sphere (caption of Figure 4) are of the same

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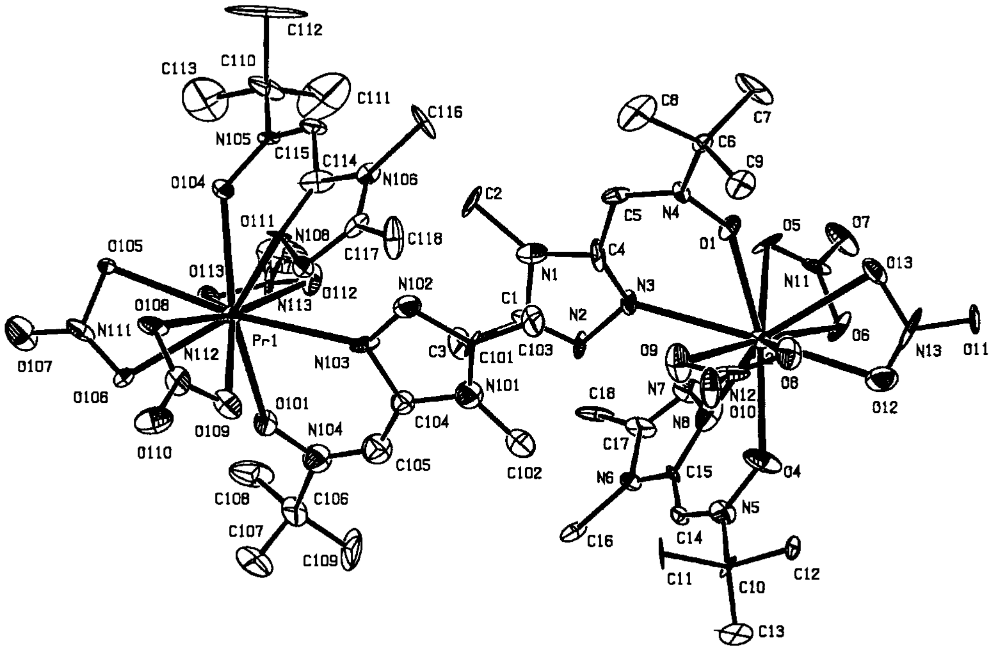

Figure 4. Molecular structure and numbering scheme for the two crystallographic independent entities of Pr(Nitrone)$_2$(NO$_3$)$_3$ (ORTEP 30% probability). The atomic labels of the entity containing Pr1 are deduced from the atomic labels of the entity containing Pr2 plus 100. Selected bond lengths (Å) and angles (deg): Pr2−O1 2.41(2), Pr1−O101 2.43(2), Pr2−O4 2.43(2), Pr1−O104 2.46(2), Pr2−N3 2.67(2), Pr1−N103 2.66(2), Pr2−N8 2.56(2), Pr1−N108 2.63(2), Pr2−ONO$_2$ 2.50(2) to 2.66(2), Pr1−ONO$_2$ 2.49(2) to 2.66(2), N4−O1 1.29(3), N104−O101 1.29(3), N5−O4 1.25(3), N105−O104 1.33(3), N4−C5 1.33(3), N104−C105 1.28(4), N5−C14 1.34(4), N105−C114 1.25(3). O1−Pr2−O4 145.1(8), O101−Pr1−O104 143.4(8), O1−Pr2−N3 64.1(7), O101−Pr1−N103 67.7(7).

order as those found for {Eu(NitTRZ)$_2$(NO$_3$)$_3$}. The shortest intermolecular distance (2.41(2) Å) is found between an O atom (O107) of a nitrato anion and an H atom (H11E; $-1 + x, y, z$) of a methyl group on the triazole unit of a neighboring molecule. The distance between two Pr(III) ions is larger than 10.2 Å. Consequently, each molecule can be considered as magnetically isolated.

In light of their molecular structures, it can be considered that the ligand field effect in {Ln(Nitrone)$_2$(NO$_3$)$_3$} and {Ln(NitTRZ)$_2$(NO$_3$)$_3$} should be very similar. Consequently, the energy spectra of the Stark sublevels for the Ln(III) ions in both compounds are very much the same. The magnetic properties of the {Ln(Nitrone)$_2$(NO$_3$)$_3$} compounds will correspond to the $\chi_{\rm Ln}$ contribution of the related Ln(III) in {Ln(NitTRZ)$_2$(NO$_3$)$_3$}. The temperature dependence of the molar magnetic susceptibility, $\chi_{\rm Ln}$, for each of the {Ln(nitrone)$_2$(NO$_3$)$_3$} compounds, Ln = Ce, Pr, Nd, Sm, Eu, Tb and Dy, was measured on a polycrystalline sample in the temperature range 2−300 K, with an applied field of 1000 Oe.

The {Ln-Radical} Interaction. For a given Ln(III) ion, the $\chi_{\rm Ln}T$ contribution obtained from {Ln(nitrone)$_2$(NO$_3$)$_3$} was mathematically subtracted from $\chi_{\rm M}^{\rm Ln}T$ measured for {Ln(NitTRZ)$_2$(NO$_3$)$_3$} to give $\Delta\chi^{\rm Ln}T$. The temperature dependence of the variation of $\Delta\chi^{\rm Ln}T = \chi_{\rm M}^{\rm Ln}T - \chi_{\rm Ln}T$ allows the nature of the interaction to be addressed. Indeed, an increase of $\Delta\chi^{\rm Ln}T$ when the temperature is lowered is indicative for ferromagnetic {Ln−radical} interactions whereas a decrease would result from antiferromagnetic interactions. To confirm the nature of the interaction provided by $\Delta\chi^{\rm Ln}T$, the field dependence of the magnetization of the two series of compounds was measured at 2 K. The experimental magnetization of each {Ln(organic radical)$_2$(NO$_3$)$_3$} compound was compared to what would be the magnetization of the corresponding uncorrelated spin system. The latter was obtained by adding to the magnetization of each {Ln(nitrone)$_2$(NO$_3$)$_3$} compound the M versus H behavior at 2 K of two $S = {}^1/_2$ radicals calculated by the Brillouin function.

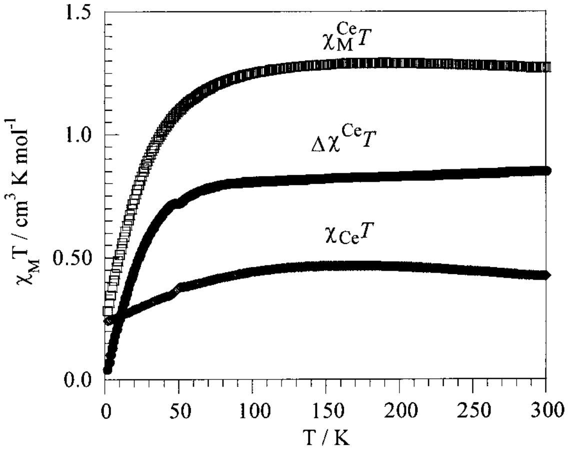

Figure 5. Temperature dependence of $\chi_{\rm M}^{\rm Ce}T$ (□), $\chi_{\rm Ce}T$ (◇), and $\Delta\chi^{\rm Ce}T$ (●).

(a) Ce (4f^1) to Eu (4f^6) Compounds. The temperature dependence of $\chi_{\rm M}^{\rm Ce}T$ and $\chi_{\rm Ce}T$ for {Ce(NitTRZ)$_2$(NO$_3$)$_3$} and {Ce(Nitrone)$_2$(NO$_3$)$_3$}, respectively, and the variation of $\Delta\chi^{\rm Ce}T = \chi_{\rm M}^{\rm Ce}T - \chi_{\rm Ce}T$ as a function of temperature are shown in Figure 5. At 300 K, $\Delta\chi^{\rm Ce}T$ is close to the value of 0.75 cm^3 K mol^{-1} expected for two noncorrelated $S_{\rm rad} = {}^1/_2$ spins and remains almost constant as T is lowered down to 50 K. Below this temperature $\Delta\chi^{\rm Ce}T$ decreases to reach 0.04 cm^3 K mol^{-1} at 2 K. The profile of the $\Delta\chi^{\rm Ce}T$ curve clearly shows that interactions exist within {Ce(NitTRZ)$_2$(NO$_3$)$_3$}. Indeed, the deviation from the paramagnetic regime below 50 K observed for $\Delta\chi^{\rm Ce}T$ can only result from the variation of the magnetic moment of the compound as a consequence of correlations between the spin carriers. The feature of $\Delta\chi^{\rm Ce}T$ as a function of temperature is characteristic for antiferromagnetic interactions. The field dependence of the magnetization of {Ce(NitTRZ)$_2$(NO$_3$)$_3$}, {Ce(Nitrone)$_2$(NO$_3$)$_3$}, and the noncorrelated

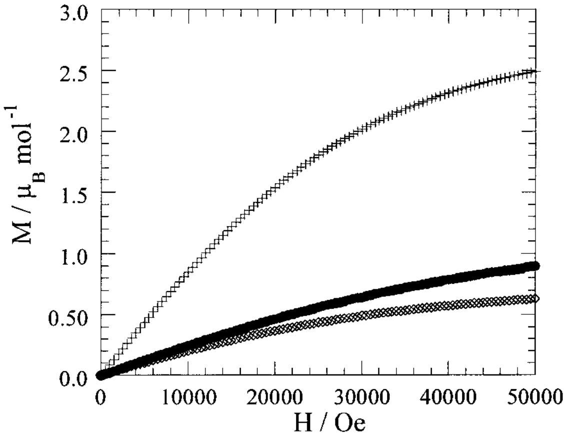

Figure 6. Experimental field dependence of the magnetization for {Ce(NitTRZ)$_2$(NO$_3$)$_3$} (●) and {Ce(Nitrone)$_2$(NO$_3$)$_3$} (◇) and calculated magnetization for the noncorrelated spin system (+) (see text).

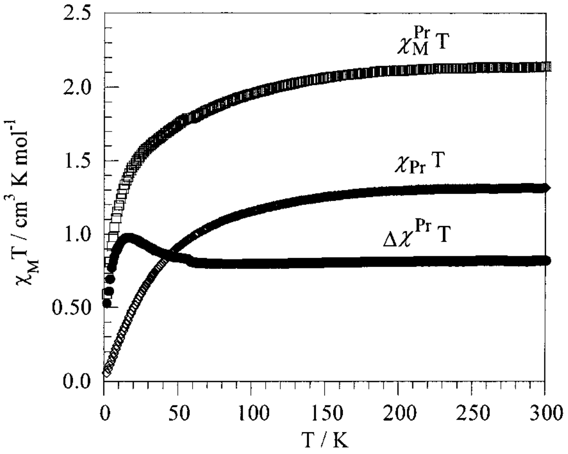

Figure 7. Temperature dependence of $\chi_M^{Pr}T$ (□), $\chi_{Pr}T$ (◇), and $\Delta\chi^{Pr}T$ (●).

spin system is shown in Figure 6. For any field, the experimental magnetization of {Ce(NitTRZ)$_2$(NO$_3$)$_3$} is lower than that of the noncorrelated system. This comparison confirms that the magnetic moment of the ground state of the compound results from antiferromagnetic interactions within the compound. The same overall behaviors were found for the Pr, Nd, and Sm compounds (see Supporting Information) showing that the ground state of these {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds arises from antiferromagnetic interactions.

The case of the Pr(III) deserves a comment. Considering the $\Delta\chi^{Pr}T$ behavior (Figure 7) it appears difficult to conclude the nature of the magnetic interaction within {Pr(NitTRZ)$_2$(NO$_3$)$_3$. Indeed, $\Delta\chi^{Pr}T$ slightly increase from 0.8 to 1.0 cm^3 K mol^{-1} when the temperature is lowered from 300 to 15 K, and then decreases to 0.5 cm^3 K mol^{-1} at 2 K. However, the magnetization experiments unambiguously show that at 2 K antiferromagnetic interactions exist in the compound.

As mentioned above, the ground state of Eu(III) is nonmagnetic, consequently the low-temperature behavior of $\chi_M^{Eu}T$ for {Eu(NitTRZ)$_2$(NO$_3$)$_3$} is mainly due to the intramolecular {radical−radical} interaction. This is confirmed by the temperature dependence of $\chi_{Eu}T$ and the perfect superimposition of the $\chi_M^{Eu}T$ and $\Delta\chi^{Eu}T$ curves at low temperature (Figure 8). Because of the nonmagnetic ground state of Eu(III) there is no Stark sublevel arising from the ground state and the magnetic behavior of {Eu(NitTRZ)$_2$(NO$_3$)$_3$} can be analyzed by a theoretical model.[22] The magnetic behavior, $\chi_M^{Eu}T$, can be attributed to the contribution of the thermal population of the excited states of the Eu(III) and the interaction between the radical units. Assuming that the interaction between the ligands is weak enough to take place at low temperature and that at this temperature only the diamagnetic ground state of Eu(III) is populated, the magnetic behavior of {Eu(NitTRZ)$_2$(NO$_3$)$_3$} can be analyzed with the expression given in eq 1. According to the intramolecular radical−radical interactions found for the La and Gd compounds[17] this assumption seams reasonable. The first term in eq 1 corresponds to the interaction within a pair of $S = {}^1/_2$ spins whereas χ_{Eu} refers to the thermal dependence of the intrinsic magnetic susceptibility of the Eu(III) ion. In this theoretical expression χ_{Eu} is given in the free-ion approximation as a function of the spin−orbit coupling parameter, λ.[22] This parameter was deduced from the temperature dependence of the magnetic behavior of {Eu(Nitrone)$_2$(NO$_3$)$_3$}. Least-squares fitting of the theoretical expression of χ_{Eu} (eq 1) gave a value of $\lambda = 371.5 \pm 0.2$ cm^{-1}. The spin−orbit coupling parameter, λ, compares well with that found previously both by luminescence and magnetic studies for a molecular coordination compound.[22]

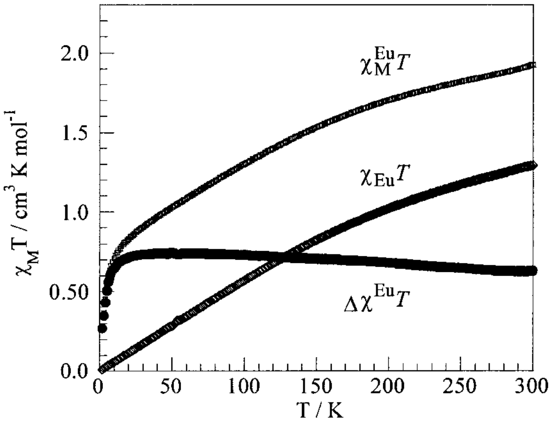

Figure 8. Temperature dependence of $\chi_M^{Eu}T$ (□), $\chi_{Eu}T$ (◇), and $\Delta\chi^{Eu}T$ (●).

$$\chi_M = \frac{2N\beta^2 g_{Rad}^2}{kT\left(3 + \exp\left(-\frac{J}{kT}\right)\right)} + \chi_{Eu} \tag{1}$$

with

$$\chi_{Eu} = \frac{\sum_{J=0}^{6}(2J+1)\chi(J)\exp[-\lambda J(J+1)/2kT]}{\sum_{J=0}^{6}(2J+1)\exp[-\lambda J(J+1)/2kT]}$$

and

$$\chi(J) = \frac{Ng^2\beta^2 J(J+1)}{3kT} + \frac{2N\beta^2(g_J-1)(g_J-2)}{3\lambda}$$

The interaction parameter, J, between organic radicals in {Eu(NitTRZ)$_2$(NO$_3$)$_3$} was determined by least-squares fitting of the expression given in eq 1 to the experimental $\chi_M^{Eu}T$ data (Figure 3). A value of $J = -3.19$ (±0.05) cm^{-1} was found (λ was fixed to 371 cm^{-1}) with a χ^2 factor[23] equal to 3×10^{-4}.

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[22] Andruh, M.; Bakalbassis, E.; Kahn, O.; Trombe, J. C.; Porcher, P. *Inorg. Chem.* **1993**, *32*, 1616−22.

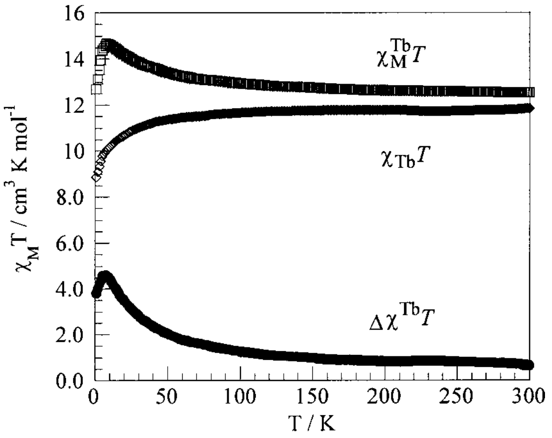

Figure 9. Temperature dependence of $\chi_M^{Tb}T$ (□), $\chi_{Tb}T$ (◇), and $\Delta\chi^{Tb}T$ (●).

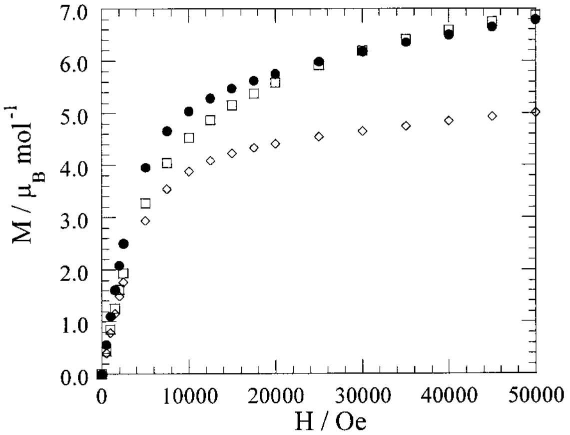

Figure 10. Experimental field dependence of the magnetization for {Tb(NitTRZ)$_2$(NO$_3$)$_3$} (●) and {Tb(Nitrone)$_2$(NO$_3$)$_3$} (◇) and calculated magnetization for the noncorrelated spin system (□) (see text).

The value found for J is comparable with the values found previously for the compounds involving diamagnetic Ln(III) ions, Y ($J = -3.1$ cm^{-1}) and La ($J = -6.8$ cm^{-1}).

(b) Tb (4f^8) and Dy (4f^9) Compounds. The temperature dependence of $\chi_M^{Tb}T$ and $\chi_{Tb}T$ for {Tb(NitTRZ)$_2$(NO$_3$)$_3$} and {Tb(nitrone)$_2$(NO$_3$)$_3$}, respectively, and the variation of $\Delta\chi^{Tb}T = \chi_M^{Tb}T - \chi_{Tb}T$ as a function of temperature are shown in Figure 9. At 300 K, $\Delta\chi^{Tb}T$ is equal to the value expected for the two noncorrelated $S = {}^1/_2$ spins. As the temperature is lowered $\Delta\chi^{Tb}T$ increases more and more rapidly reaching a maximum value of 4.6 cm^3 K mol^{-1} at 6 K before decreasing to 3.8 cm^3 K mol^{-1} at 2 K. The profile of the $\Delta\chi^{Tb}T$ curve clearly shows that ferromagnetic interactions take place within the spin carriers in {Tb(NitTRZ)$_2$(NO$_3$)$_3$}. The field dependence of the magnetization of these compounds is depicted in Figure 10. For any field before saturation the experimental magnetization curve of {Tb(NitTRZ)$_2$(NO$_3$)$_3$} is above the curve calculated for the noncorrelated system. This reveals that at 2 K, the global magnetic moment in {Tb(NitTRZ)$_2$(NO$_3$)$_3$} is higher than the sum of the contribution of the uncorrelated spin carriers. Consequently, the fundamental state of {Tb(NitTRZ)$_2$(NO$_3$)$_3$} is that for which the moments of the Tb(III) ion and of the two nitronyl nitroxides are aligned in the same direction. The {Tb−organic radical} interaction is found ferromagnetic from both the features of $\Delta\chi^{Tb}T$ and the magnetization curves. The same behavior was found for the Dy derivatives allowing the conclusion that the interactions within {Dy(NitTRZ)$_2$(NO$_3$)$_3$} are also ferromagnetic (Supporting Information, Figures S4 and S8).

Discussion

In all compounds reported so far the interaction between Gd(III), which is a 4f^7 ion, and either organic nitronyl nitroxide radicals[14,17,24,25] or Cu(II),[7−10,26−28] two $S = {}^1/_2$ spin carriers, was found to be ferromagnetic.[29] The interaction for other paramagnetic Ln(III) ions with a Cu(II) ion has been proposed[26,30] to be antiferromagnetic for those with half-filled 4f orbitals (Ce, Pr, Nd, Sm) and ferromagnetic for those with more than half-filled 4f orbitals (Tb, Dy, Ho, Er, Tm, Yb). However, examples that confirm this behavior are scarce,[19,20] mainly because the couplings involving Ln(III) ions are weak and usually are not directly accessible from the temperature dependence of the magnetic susceptibility owing to the spin−orbit coupling. Moreover, in the case of polymeric structures next-nearest-neighbor interactions might also play a role.[13] The interaction mechanism to be operating for {Gd−Cu} and {Gd−aminoxyl radical} compounds has been suggested to be the same. The question concerning the extension of this similarity between Cu(II) and nitronyl nitroxide radicals to the other paramagnetic Ln(III) ions is still open. The few {Ln−nitronyl nitroxide} complexes where Ln ≠ Gd reported so far do not allow any conclusion to be drawn about the trend of the interaction along the Ln series.[11]

The results of this study demonstrate that for the {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds the {Ln−aminoxyl radical} interaction is antiferromagnetic for the paramagnetic Ln(III) ions of the first half of the lanthanide series (Ln = Ce, Pr, Nd, Sm), whereas this interaction is ferromagnetic for the ions with more than half-filled 4f orbitals, i.e., Tb and Dy in line with the behavior previously observed for the Gd[17] and Ho[18] derivatives. All these compounds being isostructural, any influence of geometrical changes on the magnetic behavior can be excluded.

The experimental approach used to get insight into the coupling between a Ln(III) ion displaying spin−orbit coupling and its paramagnetic aminoxyl ligands is based on the knowledge of the intrinsic paramagnetic contribution, χ_{Ln}, of the metal ion. The nitrone ligands were found to be ideal diamagnetic counterparts of the paramagnetic nitronyl nitroxide-substituted triazole derivative. In the resulting {Ln(nitrone)$_2$(NO$_3$)$_3$} compound, the chemical nature of the groups coordinated to the Ln ion is the same as that in {Ln(NitTRZ)$_2$(NO$_3$)$_3$}. Moreover the X-ray structure analyses of {Pr(Nitrone)$_2$(NO$_3$)$_3$} revealed structural characteristics very similar to those found for {Eu(NitTRZ)$_2$(NO$_3$)$_3$}. The ligand field in both series of compounds should be the same, and consequently the energy spectrum of the Stark sublevels for the Ln(III) ion with either the Nitrone

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(23) Origin version 4.1;, Microcal Software: Northampton MA.

(24) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913−15.

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(28) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750.

(29) Note: After submission of this manuscript two examples of antiferromagnetic {Gd(III)-organic radical} interactions have been reported. Lescop, C.; Luneau, D.; Belorizky, E.; Guillot, M.; Rey, P. *Inorg. Chem.* **1999**, *38*, 5472. Caneschi, A.; Dei, A.; Gatteschi, D.; Sorace, L.; Vostrikova, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 246.

(30) Kahn, O.; Guillou, O. *Magnetic properties of molecular compounds containing lanthanide(III) and copper(II) ions.*; O'Connor, C. J., Ed.; World Scientific: Singapore, 1993.

or NitTRZ ligand set should be very close. This is confirmed by the magnetic behavior of the complexes in the high-temperature range. At these temperatures the spin carriers in {Ln(NitTRZ)$_2$(NO$_3$)$_3$} behave like uncorrelated paramagnetic species. The deviation of $\chi_M^{Ln}T$ versus T from a constant value arises only from the intrinsic contribution of the Ln(III) ion. The comparison of this curve with the $\chi_{Ln}T$ versus T curve obtained from the corresponding {Ln(nitrone)$_2$(NO$_3$)$_3$} derivative clearly shows that in the high-temperature range they progress concurrently as a function of temperature, i.e. the contribution of χ_{Ln} is the same for both compounds. The same conclusion can be drawn from the perfect superimposition of $\chi_M^{Eu}T$ and $\Delta\chi^{Eu}T$ versus T curves in the low-temperature range (Figure 8). Indeed, at low temperature the variation of $\chi_M^{Eu}T$ arises only from the intramolecular interaction between the paramagnetic ligands. Eu(111) having a nonmagnetic ground state. The subtraction of the intrinsic contribution of Eu(III) from $\chi_M^{Eu}T$ and should not affect these values. This is exactly what is obtained for $\Delta\chi^{Eu}T$ confirming that $\chi_{Eu}T$ deduced from the nitrone derivative is a very good approximation of χ_{Ln} occurring in {Eu(NitTRZ)$_2$(NO$_3$)$_3$}.

Both the temperature dependence of $\Delta\chi^{Ln}T = \chi_M^{Ln}T - \chi_{Ln}T$ and the magnetization as a function of the field studies are informative concerning the antiferro- or ferromagnetic nature of the interaction occurring in the {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds. The variation of $\Delta\chi^{Ln}T$ versus T reflects the variation of the magnetic moment of the molecular spin cluster as a result of the coupling between the spin carriers. Indeed, the deviation of $\Delta\chi^{Ln}T$ from the paramagnetic regime below 100 K, as observed in Figure 5 or 9 for instance, can only result from the variation of the magnetic moment of the complex as a consequence of magnetic interactions between the spin carriers. Intermolecular interactions to account for this behavior at low temperature can be excluded as they have been shown to be negligibly small (ca. -0.009 cm^{-1}) in the corresponding Gd(III) derivative.[17] The magnetization studies at 2 K provide further insight into the state of the spin system at low temperature. The comparison of the experimental magnetization of {Ln(NitTRZ)$_2$(NO$_3$)$_3$} to what would be the magnetization of the corresponding uncorrelated spin system is informative whether the magnetic moment of the molecular unit is higher or lower than that for the uncorrelated situation. A M versus H curve running below the curve of the non-correlated system is indicative of a lower magnetic moment (Figure 6). Such a situation results from antiferromagnetic interactions within the molecular spin system. An experimental magnetization larger than that of the noncorrelated system for any value of the field until saturation (Figure 10) reveals that at 2 K, the global magnetic moment in {Ln(NitTRZ)$_2$(NO$_3$)$_3$} is higher than the sum of the contribution of the uncorrelated spin carriers. Consequently, the spin state is that for which the moments of the Ln(III) ion and the two nitronyl nitroxides are aligned in the same direction, the {Ln−radical} interaction is ferromagnetic. In the series of {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds investigated both the temperature dependence of $\Delta\chi^{Ln}T$ and the magnetization as a function of the field studies clearly show that the {Ln−radical} interaction is antiferromagnetic for Ln(III) = Ce, Pr, Nd, and Sm whereas it is ferromagnetic for Ln = Gd, Tb, Dy, and Ho. The ferromagnetic interaction between the nitronyl nitroxide and the Ln(III) displaying a first-order momentum is already clearly apparent from the temperature dependence of $\chi_M^{Ln}T$ for the Tb and Dy {Ln(NitTRZ)$_2$(NO$_3$)$_3$} derivative. When Ln is Ho(III), which displays also a rather high magnetic moment at 300 K, this is not the case, $\chi_M^{Ho}T$ decreases continuously with the temperature. Two reasons could be invoked to account for such a difference. The first concerns the strength of the {Ln−radical} interaction which could be much weaker than that for the Gd to Dy derivatives. The second reason is related to the amplitude of the variation of the intrinsic contribution of the metal ion, $\chi_{Ln}T$, between the limits of the investigated temperature range. For the Tb and Dy ions the variation of $\chi_{Ln}T$ between 300 and 2 K is much less important (see Figure 9) than that for Ho(III).[18] Such a stiff decrease of $\chi_{Ho}T$ could just impose the general slope of the $\chi_M^{Ho}T$ versus T curve. The Ho compound is a typical example illustrating the difficulties to be expected for Ln(III) ions displaying a first-order orbital momentum.

Taking into account the numerous compounds for which a Gd(III) ion interacts with either aminoxyl radicals or Cu(II) ions, it appears that neither the coordination number of the metal ion nor the topology of the compound affect the nature of the coupling, which was always found to be ferromagnetic. If this applies for the other Ln(III) ions, the nature of the interactions found in this study for the {Ln(NitTRZ)$_2$(NO$_3$)$_3$} compounds should remain the same for related {Ln−aminoxyl} derivatives. Interestingly, the results provided by this study compare well with the nature of the {Ln(III)−Cu(II)} interactions reported recently. Indeed, for the compounds involving Ln(III) ions from the first half of the lanthanide series the interaction was found to be antiferromagnetic. The comparison is more tricky for the Ln(III) ions with more than half-filed f-orbitals because the results reported for the {Ln−Cu} compounds are not consistent for the ions after Dy(III).[19,20] Nevertheless, the trend seems to be the same as that described here for the {Ln−aminoxyl} interactions. It appears that the similarity observed already between an aminoxyl radical and Cu(II) in the interaction with Gd(III) can be extended to the other paramagnetic Ln(III) ions. Consequently, there is clear evidence that the interaction mechanism propose for the {Ln−Cu} interaction applies also to the {Ln−aminoxyl} interaction.

Two pathways might be invoked to account for the intramolecular antiferromagnetic radical−radical interaction observed for {Eu(NitTRZ)$_2$(NO$_3$)$_3$}. The first is to consider an interaction through the NO$_3^-$ anion located between the two radical moieties, and the second is via the metal center. A comparison of the calculated interaction parameter J for the Eu derivative (-3.19 cm^{-1}) with the values found previously for the corresponding compounds involving either diamagnetic Ln(III) ions, Y (-3.1 cm^{-1}) and La (-6.8 cm^{-1}) or Gd (-7.0 cm^{-1}), shows the differences between the magnetic properties of these compounds. These compounds are isomorphous, consequently a radical−radical interaction through the NO$_3^-$ anion should yield almost the same interaction parameter; this is clearly not the case. The main difference between these compounds is the nature of the metal center. The observation of different J values corroborates the hypothesis that the metal center may be involved in the superexchange pathway between the two radicals.[11,27]

The approach we used to investigate the nature of the {Ln−radical} interaction provides conclusive but only qualitative information. To get insight into the strength of these interactions accurate models describing both the intrinsic contribution, χ_{Ln}, of the Ln(III) ions displaying spin−orbit coupling and the magnetic exchange interactions of each of the levels arising from the energy spectrum of the Stark sublevels with the spin carrier interacting with the Ln(III) ion have to be developed.

Conclusion

For the first time, conclusive information concerning the nature of the interactions involving nitronyl nitroxide radicals and Ln(III) ions displaying spin−orbit coupling is provided. A systematic investigation of an isostructural series of compounds permitted the evolution of these interactions to be compared as a function of the electronic configuration of the 4f orbitals. For the Ln(III) with $4f^1$ to $4f^5$ electronic configurations the {Ln−organic radical} interaction is antiferromagnetic. Conversely, this interaction was found ferromagnetic for the configurations $4f^7$ to $4f^{10}$.

Experimental Section

General Considerations. All reactions were performed using 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,[31] the Nitrone,[18] and $Ln(NO_3)_3,xH_2O$[16] were prepared as described in the literature. Elemental analyses were conducted by the central CNRS microanalysis service (Vernaison). Magnetic susceptibility data were measured at 1000 Oe field strength with a SQUID MPMS-5S magnetometer working down to 2 K.

Crystallographic Data Collection and Structure Determination. Single crystals of {Ln(NitTRZ)$_2$(NO$_3$)$_3$} were mounted at the end of a glass fiber. Cell dimensions and orientation matrix for data collection were obtained at −10 °C from least-squares refinement using the setting angles of 25 centered reflections. Intensity data were collected at −10 °C on an Enraf-Nonius CAD-4 diffractometer using a Mo Kα (λ = 0.71073 Å) radiation source. After a semi-empirical ψ-scan[32] absorption correction, the data reduction was performed using MolEN[33] while structure solutions and refinements were carried out using the SHELXS-86 and SHELXL-97 programs.[34,35] Hydrogen atoms were located on the basis of geometrical consideration and treated according to the riding model during refinement with isotropic displacement corresponding to the heavy atom they are linked to. Crystallographic and refinement parameters are given in Table 1. The highest positive electron density of 2.15 is located at less than 1 Å from the heavy atom.

A small single crystal of {Pr(Nitrone)$_2$(NO$_3$)$_3$} of approximate dimensions $0.10 \times 0.10 \times 0.10$ mm^3 was used to perform the intensity data collection. The cell parameters were obtained from the angles of 25 reflections ($9.2 < 2\theta < 20.6°$). The data collection was based on $\omega/2\theta$ scans. The crystal structure was solved with direct methods using SHELXS and refined using SHELXL-97 programs.[34,35] Refinements of the atomic parameters conducted with a data file corrected from absorption correction using semi-empirical Ψ-scans and a data file not corrected from absorption correction gave no noticeable differences, probably due to the size of the chosen single crystal. Moreover, the crystal structure was solved and refined in both the $P\bar{1}$ and $P1$ space groups to remove the well-known ambiguity between these two space groups.[36] The highest R-factor values as well as the noncoherent bond length and angle values obtained in the centered space group confirmed our choice of the $P1$ space group. Despite the high number of atoms in the asymmetric unit, the ratio between the number of reflections observed (3724) and the number of atomic parameters to refine (739) appears reasonable (around 5). The butyl carbon atoms of the ligand extremities are affected by a strong thermal motion.

{Ln(NitTRZ)$_2$(NO$_3$)$_3$}: All compounds were synthesized and crystallized as described previously for Gd.[17] Analyses were calculated for {$C_{22}H_{36}N_{13}O_{13}Ln$, X solvent}, calcd (found). **Ce**: 2 H_2O: C, 30.49 (30.58), H, 4.65 (4.72); N, 21.00 (21.81). **Pr**: C, 31.78 (31.9), H, 3.36 (4.42); N, 21.90 (21.75). **Nd**, 2MeCN: C, 34.06 (33.99); H, 4.62 (4.71); N, 22.9 (21.66). **Sm**, 3H_2O: C, 29.52 (29.41); H, 4.73 (4.38); N, 20.34 (20.23). **Eu**: C, 31.36 (31.52); H, 4.31 (4.66); N, 21.61 (21.77). **Tb**, 1.5MeCN: C, 32.96 (33.13); H, 4.48 (4.47); N, 22.29 (22.12). **Dy**, 1MeCN: C, 32.44 (32.04); H, 4.40 (4.39); N, 21.93 (21.43).

{Ln(Nitrone)$_2$(NO$_3$)$_3$}: All compounds were prepared by the same procedure. For example, in a tipical synthesis, a solution of Nitrone (100 mg, 0.5 mmol) and $Ce(NO_3)_3{\cdot}6H_2O$ (110 mg, 0.25 mmol) in MeOH (15 mL) was stirred for 6 h at room temperature. The solvent was then removed in vacuo and the residue washed with CH_2Cl_2. The solid was dissolved in MeCN and the solution allowed to diffuse in Et_2O or thf to give microcrystalline needles. IR (KBr, cm^{-1}): 2986 (w), 1607 (m), 1537 (m), 1472 (s), 1384 (s), 1369 (s), 1319 (s), 1150 (m), 1083 (w), 1033 (w), 924 (m).

Analyses were calculated for {$C_{18}H_{32}N_{11}O_{11}Ln$, X solvent}, calcd (found). **Ce**, 2H_2O: C, 28.65 (28.16); H, 4.80 (4.66); N, 20.41 (20.12). **Pr**: C, 30.05 (30.11); H, 4.48 (4.67); N, 21.41 (21.15). **Nd**, 1MeOH: C, 30.23 (30.38); H, 4.81 (4.65); N, 20.41 (20.46). **Sm**, 2H_2O: C, 28.26 (28.30); H, 4.74 (4.60); N, 20.14 (19.97). **Eu**, 5H_2O: C, 26.35 (25.9), H, 5.16 (4.37); N, 18.78 (19.0). **Tb**, 1MeOH, 2.5 H_2O: C, 28.01 (28.04); H, 5.07 (4.33); N, 18.91 (18.30). **Dy**: C, 29.17 (29.02); H, 4.35 (4.37); N, 20.79 (20.59).

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Supporting Information Available: Temperature dependence of $\chi_{\mathrm{Ln}}T$ (Ln = Nd, Sm, Dy) and field dependence of the magnetization (Ln = Pr, Nd, Sm, Dy) for {Ln(Nitrone)$_2$(NO$_3$)$_3$}; temperature dependence of $\chi_{\mathrm{M}}^{\mathrm{Ln}}T$ (Ln = Ce, Pr, Nd, Sm), temperature dependence of $\Delta\chi^{\mathrm{Ln}}T$ (Ln = Nd, Sm, Dy), and field dependence of the magnetization (Ln = Pr, Nd, Sm, Dy) for {Ln(NitTRZ)$_2$(NO$_3$)$_3$} (PDF). X-ray crystallographic files, in CIF format, for {Eu(NitTRZ)$_2$(NO$_3$)$_3$} and {Pr(Nitrone)$_2$(NO$_3$)$_3$}. This material is available free of charge via the Internet at http://pubs.acs.org.

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