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Magnetic Properties of Lanthanide Complexes with Nitronyl Nitroxides

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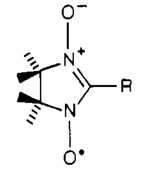
Europium(III) and gadolinium(III) hexafluoroacetylacetonates, M(hfac)$_3$, form stable bis adducts with nitronyl nitroxides (2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide, NITR; R = phenyl, ethyl). The magnetic properties of Gd(hfac)$_3$(NITPh)$_2$ were investigated in the range 1.1-300 K, while all the other compounds were studied in the range 4-300 K. The gadolinium(III) ions were found to be weakly coupled in a ferromagnetic fashion to the radical, while the radicals are antiferromagnetically coupled to each other. The possible mechanisms responsible for this behavior are discussed.

Many efforts have currently been devoted to the synthesis of materials with expected magnetic properties. In order to arrive at such a result, chemists must have available different building blocks with which it will be possible to arrange complex architectures. Therefore, it is of fundamental interest to know the conditions under which, for instance, ferro- or antiferromagnetic coupling will be developed between different spins, and simple molecular clusters need to be synthesized and investigated in order to test theories. This procedure is now fairly well established for transition-metal ions,[2,3] but much less is known for lanthanide ions. Indeed, although lanthanides have long been known to develop interesting magnetic properties when used to dope transition-metal ionic lattices,[4-8] the study of discrete magnetically coupled molecular systems has been largely overlooked up to the present.

Some of us have recently reported the magnetic properties of trinuclear complexes containing one gadolinium(III) and two copper(II) ions magnetically coupled in such a fashion that a smooth increase of χT on lowering T was observed.[9-12] These data were explained with an isotropic ferromagnetic exchange between the gadolinium and the copper ions. The coupling must be determined by superexchange through the oxygen bridges, but no attempt was made to use an orbital model to justify the observed coupling. This purpose in principle might be achieved more easily by studying the interaction of lanthanide ions with stable organic radicals such as nitroxides, because in this case the magnetic interaction would be of the direct exchange type, and the observed coupling might be directly connected with the nature of the bond interaction between the π^* orbital on the ligand and the f orbitals of the lanthanides. In other words, the nitroxides, which are widely used as spin labels and spin probes, in this case might be used as bond probes,[13] in the sense that an analysis of their interaction with the metal ions should provide first-hand information on the metal-ligand bond and on the nature of the magnetic orbitals.

With these considerations in mind, we synthesized a series of stable adducts of lanthanides with nitronyl nitroxides of general formula



We already used these ligands with transition-metal ions and observed many different and novel magnetic properties.[14-16] These lanthanide adducts are, to the best of our knowledge, the first solid derivatives of this kind that are fully characterized, although some data are available in the literature for such adducts in solution. We wish to report here the magnetic properties of M(hfac)$_3$(NITR)$_2$ (hfac = hexafluoroacetylacetonate; NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide; R = phenyl, ethyl; M = Eu, Gd). The reason of the choice of europium and gadolinium lies in the relative simplicity of their magnetic properties, which do not show large anisotropy effects like the other lanthanides.

Experimental Section

Compound Preparation. The NITR radicals were prepared according to the literature method[19,20] and identified by melting point and EPR and ^{1}H NMR spectra.[21,22]

All the M(hfac)$_3$(NITR)$_2$ derivatives were prepared by following the procedure reported elsewhere[23] and satisfactorily analyzed for C, H, and N.

Physical Measurements. The magnetic susceptibilities were measured with different techniques. For the experiments in the 4.2-300 K range a SHE superconducting SQUID magnetometer operating at a field strength of 0.5 T and an Aztec DSM5 susceptometer equipped with a Bruker BE-15 electromagnet operating at 1.35 T were used. The measurements in the 1.1-4.2 K range were performed on an ac mutual inductance bridge with zero field.

A single crystal of Eu(hfac)$_3$(NITPh)$_2$ was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer with monochromatized Mo Kα radiation. Accurate cell constants were derived from a least-squares refinement of the setting angles of 25 reflections. They were found to be a = 1165.7 (4) pm, b = 1272.6 (5) pm, c = 1909.5 (3) pm, α = 87.54 (3)°, β = 73.20 (2)°, and γ = 85.68°.

Results and Discussion

The high-temperature magnetic data of Gd(hfac)$_3$(NITPh)$_2$ were previously reported.[23] In Figure 1 we show χ^{-1} vs T and χT vs T data in the 1.1-4.2 K range. A least-squares analysis of the χ^{-1} vs T curve yields the Curie constant C = 10.23 emu mol^{-1} K and Θ = -3.1 K, indicating a weak antiferromagnetic coupling as confirmed by the χT curve, which decreases on lowering the temperature. The C value is larger than expected for one S =

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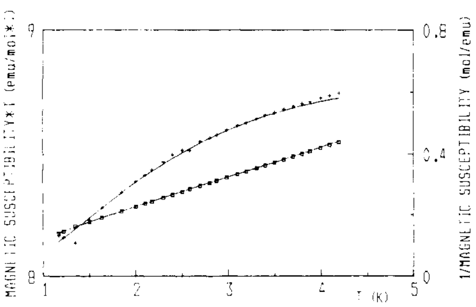

Figure 1. Temperature dependence of the inverse molar magnetic susceptibility χ_m^{-1} (□) and of the product $\chi_m T$ (+) of Gd(hfac)$_3$(NITPh)$_2$ in the range 1.2–4.2 K. The curves are calculated as described in the text.

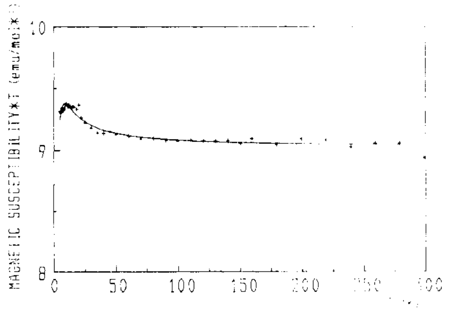

Figure 2. Temperature dependence of the product $\chi_m T$ (+) for Gd(hfac)$_3$(NITPh)$_2$ in the range 4.2–300 K. The curve is calculated as described in the text.

$^7/_2$ and two $S = {}^1/_2$ uncoupled spins, 8.625 emu mol^{-1} K, and smaller than anticipated for fully coupled spins within the Gd(hfac)$_3$(NITPh)$_2$ molecules, 12.375 emu mol^{-1} K.

The high-temperature data for Gd(hfac)$_3$(NITEt)$_2$ are shown in Figure 2. χT increases on decreasing the temperature to reach the highest value of 9.17 emu mol^{-1} K at 5.05 K.

The temperature dependence of the magnetic susceptibility of Eu(hfac)$_3$(NITPh)$_2$ and Eu(hfac)$_3$(NITEt)$_2$ is shown in Figure 3. Both curves go through a maximum at ca. 15 K.

The structure of Gd(hfac)$_3$(NITPh)$_2$ has been previously determined,[23] and the coordination around the gadolinium ion has been found to be distorted dodecahedral.[23] Eu(hfac)$_3$(NITPh)$_2$ has been found to be strictly isomorphous with the gadolinium analogue, and we assume that it is also isostructural. The structure of the NITEt derivatives is not known, but we assume that it is similar to that of the NITPh complexes on the basis of the similarity of the physical properties and in particular of the magnetic ones.

Gadolinium(III) has a $^8S_{7/2}$ ground state, and the excited states are well separated in energy. Therefore, its magnetic interactions with the radicals can be well described by isotropic exchange interaction. We already suggested a model to analyze the magnetic behavior of a system containing one gadolinium and two radicals in which a $S = {}^7/_2$ spin is interacting with two $S = {}^1/_2$ spins.[10-12] The model uses a Hamiltonian of the type

$$\mathcal{H} = J(\mathbf{S}_{Gd}\cdot\mathbf{S}_{rad1} + \mathbf{S}_{rad2}\cdot\mathbf{S}_{Gd}) + J'\mathbf{S}_{rad1}\mathbf{S}_{rad2}$$

The cluster of three spins has been considered as symmetric, because the gadolinium–radical distances are very close to each other (232.7 (5) and 233.7 (5) pm, respectively[23]) and also the metal–oxygen–nitrogen angles, which have been found to have large influences on the magnetic coupling,[24] are very similar to each other (141.1 and 144.6°, respectively). The magnetic structure of the trimer consists of four energy levels, one with $S = {}^9/_2$, two with $S = {}^7/_2$, and one with $S = {}^5/_2$. Since all these states have a high spin multiplicity, the influence of the magnetic field, especially at low temperature, can play an important role in determining the magnetic behavior of these type of compounds.

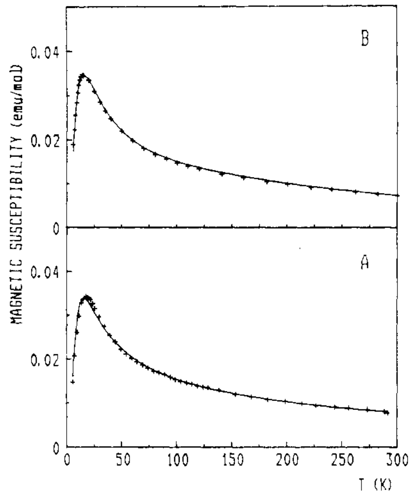

Figure 3. Temperature dependence of the molar magnetic susceptibility χ_m for Eu(hfac)$_3$(NITPh)$_2$ (A) and for Eu(hfac)$_3$(NITEt)$_2$ (B) in the range 4.2–300 K. The curves are calculated as described in the text.

Therefore, we decided to account for the magnetic field strength to make possible a comparison of our data, which were obtained with different techniques in different magnetic fields. The final expression for the magnetic susceptibility is

$$\chi = \frac{N\sum_i g\mu_B S(2S + 1)e^{-E_i/kT}[B(\eta)]}{3kTHZ}$$

where N is the Avogadro number, S is the spin of the ith state of energy E_i, H is the magnetic field, Z is the partition function, $\eta = g\mu_B H/kT$, and $B(\eta)$ is the Brillouin function defined as

$$B(\eta) = 1/S[(S + 1/2)\coth(S + 1/2)\eta - 1/2\coth(\eta/2)]$$

The experimental data were fitted with this expression with a minimization procedure based on a standard MINUIT library.[25] The minimized function is $R = [\sum(\chi T_{obs} - \chi T_{calc})^2/\sum(\chi T_{obs})^2]^{1/2}$. The best-fit values are $g = 2.029$ (3), $J = -1.23$ (5) cm^{-1}, and $J' = 5.1$ (7) cm^{-1} for the NITPh derivative and $g = 2.049$ (2), $J = -0.50$ (4) cm^{-1}, and $J' = 4.3$ (6) cm^{-1} for the NITEt one, with agreement factors 3.73×10^{-3} and 3.55×10^{-3}, respectively. The values of the parameters calculated for Gd(hfac)$_3$(NITPh)$_2$ are slightly different from those previously reported,[23] the difference being due to the neglect of the magnetic field effects in the previous calculation.

These data require a fairly strong antiferromagnetic interaction between the radicals. Since it is well-known that the exchange interaction between terminal spins in linear three-spin clusters is determined with only moderate accuracy due to the large correlation between the J and J' parameters,[26] we decided to investigate the behavior at lower temperature for at least one of the compounds because in this range the effects of J' should be more significant.

The low-temperature data for Gd(hfac)$_3$(NITPh)$_2$ were separately fit, and they yielded $g = 2.027$ (3), $J = -1.17$ (5) cm^{-1}, and $J' = 6.8$ (8) cm^{-1} with $R = 4.81 \times 10^{-3}$. The agreement of these parameters with those obtained from the high-temperature data can be considered as satisfactory, because g and J are equal within error, and J', which is determined only with moderate accuracy, is equal to the high-temperature value within 2 standard deviations.

These data confirm the weak ferromagnetic nature of the exchange interaction between gadolinium(III) and the radical and compare well with the data reported for gadolinium(III)–copper(II) pairs.[9-12] In order to envisage the possible exchange mechanisms, it is necessary to consider the overlaps between the magnetic orbitals on the metal ion and the radicals, respectively.

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A simple angular overlap analysis[27] shows that, for the geometry observed in the X-ray crystal structure, the metal orbitals which are mainly involved in the interaction are a linear combination of $(4z^2 - x^2 - y^2)x$ and $(3x^2y - y^3)$ orbitals for one radical and of $(4z^2 - x^2 - y^2)y$ and $(x^3 - 3xy^2)$ for the other. The other metal orbitals are essentially orthogonal to the π^* orbitals; therefore, they are expected to give ferromagnetic contributions. Apparently the latter are enough to overcome the antiferromagnetic interaction determined by the nonzero overlap, which must be in any case fairly small.

In principle it might be assumed that also a dipolar interaction might yield a parallel alignment of the metal and radical spins.[3,28] However, the required values of the dipolar tensor, $\mathbf{D}_{\mathrm{dip}}$, are much higher than would be expected on the basis of the point dipolar model, which gives a D value of 0.2 cm^{-1} calculated for a interacting distance of 233 pm: therefore, we definitely prefer the interpretation with the isotropic exchange model. As far as the coupling between the radical spins is concerned, we defer the discussion after the analysis of the data of the europium(III) derivatives.

Europium(III) has a ground $^7F_0$ level and excited states $^7F_1$ and $^7F_2$ at ca. 350 and 1000 cm^{-1}, respectively. The magnetic susceptibility of isolated europium ions is expected to increase on decreasing the temperature and to reach a constant value at relatively low temperature, due to the field-determined admixture of the excited states into the ground nonmagnetic state.[29] The actual value of the susceptibility depends essentially (neglecting $^7F_2$) on the energy separation $^7F_0$–$^7F_1$ and on the splitting of the excited triplet. The ground state $^7F_0$ is coupled to the radical spins, yielding a singlet and a triplet, while the excited state $^7F_1$ yields a quintet, two triplets, and a singlet. However, since $^7F_1$ has large unquenched orbital angular momentum, the exchange interaction is expected not to be isotropic and the total spins are not good quantum numbers. Therefore, it is not possible to use the Heisenberg–Dirac–Van Vleck Hamiltonian to describe the interaction of $^7F_1$ with radicals, but anisotropy effects must be explicitly taken into account. However, if we assume that this interaction is small compared to the $^7F_0$–$^7F_1$ separation and consider that the resultant levels are populated only at high temperatures, it is possible to attempt to reproduce the magnetic susceptibility of the $\mathrm{Eu(hfac)_3(NITR)_2}$ complexes including only the low-symmetry fields felt by europium(III) and the radical–radical interactions which can be described by an isotropic Hamiltonian.

The appropriate Hamiltonian therefore can be written in the form

$$\mathcal{H} = \mathcal{H}_{\mathrm{Eu}} + \mathcal{H}_{\mathrm{rad-rad}}$$

The single-ion Hamiltonian of Eu can be conveniently expressed by using the operator equivalent formalism:[30]

$$\mathcal{H}_{\mathrm{Eu}} = \lambda L{\cdot}S + \frac{2}{45}\sum_m \mathrm{A}_2^m\langle r^2\rangle \mathrm{O}_2^m(\mathrm{L}) - \frac{2}{495}\sum_m \mathrm{A}_4^m\langle r^4\rangle \mathrm{O}_4^m(\mathrm{L}) + \frac{4}{3861}\sum_m \mathrm{A}_m^6\langle r^6\rangle \mathrm{O}_m^6(\mathrm{L})$$

$\mathcal{H}_{\mathrm{rad-rad}}$ is simply given by

$$\mathcal{H}_{\mathrm{rad-rad}} = J\mathbf{S}_{\mathrm{rad1}}{\cdot}\mathbf{S}_{\mathrm{rad2}}$$

The appropriate basis set for $\mathcal{H}$ can be that given by the direct product functions $|33JM,{}^1/_2M',{}^1/_2M''\rangle$, where 3 corresponds to S and L and $J = 0, 1$ for the two lowest levels of the europium ion, and the additional quantum numbers refer to the two radicals. The symmetry of the lanthanide ion is C_1 in the crystal structure; however, we assume an approximate C_{2v} symmetry for the sake of reducing the number of parameters. In this way we have to include only operators with $n = 0, 2, 4$, and 6. If we further assume that the role of therms with $n \geq 4$ can be neglected, then we are left only with three crystal field parameters and the isotropic coupling constant for the interaction between the radicals.

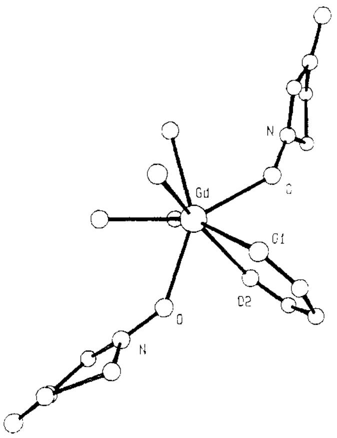

Figure 4. Schematic view of the coordination sphere of gadolinium in $\mathrm{Gd(hfac)_3(NITPh)_2}$. For the sake of clarity, with the oxygen atoms directly bound to the metal, only the skeletons of the two nitronyl nitroxides and of the hexafluoroacetylacetonate molecule containing the O1 and O2 atoms are shown.

The experimental susceptibility curves were fitted with the above model to yield $\lambda = 274.7\ \mathrm{cm}^{-1}$, $A_2^0\langle r^2\rangle = -362.2\ \mathrm{cm}^{-1}$, $A_2^2\langle r^2\rangle = -39.9\ \mathrm{cm}^{-1}$, and $J_{\mathrm{rad-rad}} = 17.6\ \mathrm{cm}^{-1}$ for $\mathrm{Eu(hfac)_3(NITPh)_2}$ with an agreement factor $R = 1.64 \times 10^{-2}$ and $\lambda = 290.3\ \mathrm{cm}^{-1}$, $A_2^0\langle r^2\rangle = -339.5\ \mathrm{cm}^{-1}$, $A_2^2\langle r^2\rangle = -26.8\ \mathrm{cm}^{-1}$, $J_{\mathrm{rad-rad}} = 16.3\ \mathrm{cm}^{-1}$ for $\mathrm{Eu(hfac)_3(NITEt)_2}$ with $R = 7.18 \times 10^{-3}$. The crystal field parameters for europium are a little bit different from those usually accepted for this ion in octahedral symmetry.[30-32] However, it must be underlined that the present compound has a dodecahedral coordination and the order of the levels might be indeed different. Recent experimental work on luminescence spectra of europium(III) complexes have indeed shown that the $^7F_1$ levels can undergo largely different splittings depending on the crystal field.[33,34]

The other relevant parameter that emerges from the analysis of the magnetic susceptibility of $\mathrm{Eu(hfac)_3(NITR)_2}$ is the relatively strong antiferromagnetic coupling between the radical spins, which is responsible for the maximum of χ observed at ca. 15 K. In the model that we have used, the coupling is intramolecular in nature and we have accurately determined in the crystal structure of $\mathrm{Gd(hfac)_3(NITPh)_2}$ that no short intermolecular contact is present.[23] Indeed, the shortest Gd–Gd distance is 1038 pm, and the free NO group of a radical is 487 pm from the next nearest neighbor, so that it must be excluded that these contacts are responsible for the large coupling experimentally observed. The extent of the coupling between the radicals is certainly surprising. In order to check that this interpretation does not suffer from the assumption that the coupling between europium and radicals can be neglected, we relaxed it and considered the effect of an isotropic coupling between Eu and NITR in the excited state on the energies of the ground-state manifold of four levels. We found that indeed also small values of $J_{\mathrm{Eu-rad}}$ can affect the ground levels, but the effect is that of lowering the ground triplet compared to the singlet, a result that would require an even larger radical–radical interaction to justify the experimental maximum in χ at ca. 15 K.

We previously observed an intermolecular antiferromagnetic coupling of 15 cm^{-1} between nitroxides in a copper radical complex,[14] but the distance between the NO groups was 356 pm and they were oriented in such a way to give maximum overlap between the π^* orbitals. Similar contacts in nickel and cobalt complexes in which the distance between the NO groups is 312.7

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pm yielded $J = 2\ \mathrm{cm^{-1}}$ only.[16] In Eu(hfac)$_3$(NITR)$_2$ the distance between the NO groups bonded to the metal ion must be close to 436 pm, the value observed in the gadolinium derivative.[23] Again this distance seems to be too long to justify the coupling through the direct overlap of the π^* orbitals. Therefore, a mechanism must be operative through either the metal orbitals or the hfac ligands.

The involvement of the hfac orbitals may be suspected for the moiety containing the O1 and O2 oxygen atoms (Figure 4), whose plane is almost orthogonal to the planes of the two nitroxides. The distances of the oxygen atoms of the nitroxides from the atoms of this hfac molecule range from 273 to 374 pm so that some overlap, leading to antiferromagnetic coupling, may be anticipated. If this mechanism were the only one operative, the observed coupling should be very similar in both the europium and gadolinium derivatives. The values we calculate for Gd(hfac)$_3$(NITR)$_2$ are smaller than those of Eu(hfac)$_3$(NITR)$_2$, but the relative uncertainty in the determination of the parameters for the former does not allow us to reach any firm conclusion about the involvement of the metal orbitals.

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Registry No. Eu(hfac)$_3$(NITEt)$_2$, 117800-31-4; Gd(hfac)$_3$(NITPh)$_2$, 11015-58-0; Gd(hfac)$_3$(NITEt)$_2$, 117800-32-5; Eu(hfac)$_3$(NITPh)$_2$, 117800-33-6.

Contribution from the Department of Chemistry, University of Florence, Florence, Italy, and Department de Recherche Fondamentale, Centre d'Etudes Nucleaires, Grenoble, France

Structure and Magnetic Properties of Linear-Chain Complexes of Rare-Earth Ions (Gadolinium, Europium) with Nitronyl Nitroxides

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Gd(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate, NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) crystallizes in the monoclinic space group $P2_1/n$ with cell parameters $a = 2006.4$ (4) pm, $b = 1706.4$ (4) pm, $c = 2267.3$ (2) pm, $\beta = 113.82$ (1)°, $V = 7101.3 \times 10^6$ pm^3, $Z = 4$, and $R_w = 0.076$. The crystal structure consists of linear chains made by Gd(hfac)$_3$ moieties linked by bridging nitroxide radicals. The magnetic behavior shows the presence of an antiferromagnetic coupling. Several models for interpreting the magnetic structure are proposed and discussed.

Low-dimensional magnetic materials have been the focus of very active research in the last years, because their properties are in principle much easier to treat theoretically than three-dimensional systems.[2] The combined efforts of physicists and chemists have produced a large number of new classes of materials, such as ferromagnetic chains,[3,4] ferrimagnetic chains,[5,6] alternating chains,[7,8] two-dimensional ferromagnets and antiferromagnets, etc. Most of these materials are formed by transition-metal ions, both in ionic and in molecular lattices, but also organic radicals are well represented.

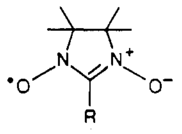
Low-dimensional materials containing lanthanide ions on the other hand are practically nonexistent, as reported in a popular textbook on magnetochemistry:[9] "there appear to be no low dimensional rare earth compounds". This result is rather unfortunate because the large anisotropy effects associated with the unquenched orbital angular momenta of the lanthanides might in principle yield interesting magnetic phenomena.

Table I. Crystallographic Data for Gd(hfac)$_3$NITEt

Gd$_2$C$_{48}$H$_{40}$F$_{36}$N$_4$O$_{16}$	fw = 1927.30
$a = 20.064$ (4) Å	space group: $P2_1/n$
$b = 17.064$ (4) Å	$T = 21.4$ °C
$c = 22.673$ (2) Å	$\lambda = 0.7107$ (Mo Kα)
$\beta = 113.82$ (1)°	$\rho = 1.80$ g cm^{-1}
$V = 7101.3$ Å	$\mu = 19.71$ cm^{-1}
$Z = 4$	$R(F_o) = 0.0854$
	$R_w(F_o) = 0.0763$

Very recently the new ceramic high-T_c superconductors have somewhat modified the negative picture because it has been suggested that when yttrium is substituted by magnetic rare-earth ions these form a two-dimensional magnet.[10,11]

We have recently reported that nitronyl nitroxides, NITR, stable organic radicals that have the general formula



R = C$_6$H$_5$.CH$_3$.CH$_2$CH$_3$

can form with transition metal ion linear-chain compounds[3,5] and two-dimensional materials.[12]

Trying to synthesize analogous compounds with the rare-earth ions appeared therefore to be a natural extension. We wish to

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