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Magnetic Interactions and Magnetic Ordering in Rare Earth Metal Nitronyl Nitroxide Chains

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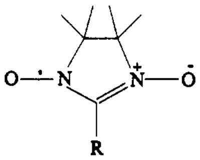
The magnetic behavior of a series of compounds with general formula RE(hfac)$_3$NITEt (RE = Tb, Er, Ho; hfac = hexafluoracetylacetonate; NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) are reported. The presence of lanthanide ions with anisotropic ground states deeply influences the magnetic behavior of these low-dimensional systems. In particular magnetic phase transitions to ordered states are observed. The nature of these transitions is analyzed and the unusually high critical temperatures are related to the anisotropy of the rare earth metal ions. The coupling mechanisms are reconsidered in comparison with those discussed for similar systems where diamagnetic or isotropic metal ions are present.

Introduction

Various kinds of molecular magnetic materials are currently being investigated, and among them systems containing rare earth metal ions are attracting interest.[1,2] In fact it has been found that the magnetic interactions between rare earth metal ions and copper ions or between rare earth metal ions and organic radicals are far from negligible and are ferromagnetic in nature in many cases.[3–13] Furthermore in several instances next-nearest-neighbor interactions had to be taken into consideration in order to interpret the experimental data.[14–16] This is particularly relevant in the case of linear chain compounds in which rare earth metal ions alternate regularly in space with nitronyl nitroxide radicals, NITR:



The NITR radicals have been widely used with transition metal ions to yield magnetic materials.[17] In particular it was found that linear chains in which NITR radicals and manganese(II)[18] or nickel(II)[19] ions alternate in space behave as one-dimensional ferrimagnets which order as bulk ferrimagnets below 10 K, while when the metal ions are copper(II) they behave as one-dimensional ferromagnets.[20] For the copper compounds no magnetic ordering was observed above 1.2 K.

The behavior of one-dimensional compounds formed with rare earth ions is completely different: when RE = Gd(III), a Heisenberg ion with $S = {}^7/_2$ ground state, it was reported that the temperature dependence of the magnetic susceptibility approximates more closely the behavior of an antiferromagnet rather than that of a ferro- or a ferrimagnet.[14,16] This is surprising, because in the limit of nearest-neighbor interactions only, with two different spins such as $S = {}^7/_2$ of gadolinium and $S = {}^1/_2$ of the radical, a ferromagnet is expected for parallel alignment of the spins, and a ferrimagnet, for antiparallel alignment of the spins.

We originally proposed that this anomalous behavior may be due to dominant next-nearest-neighbor interactions and proposed a simplified Ising treatment in order to substantiate this claim.[16] Although acceptable agreement was obtained with the experimental data, it is apparent that gadolinium is an inappropriate ion to model with an Ising approach. Therefore we tried other anisotropic rare earth metal ions in order to provide additional evidence for our model.

We have found that Dy(hfac)$_3$NITEt (hfac = hexafluoroacetylacetonate and NITEt = 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) has an overall antiferromagnetic behavior, but even more interestingly, it undergoes a magnetic phase transition at ca. 4 K, ordering as a weak ferromagnet.[21,22] This is a very surprising result, considering that the material has a one-dimensional structure and that the chains are well shielded one from the other. For comparison, the Mn(hfac)$_2$NITR compounds, which have similar chain structures and a strong intrachain antiferromagnetic coupling of ca. 400 K, order magnetically at ca. 8 K.

It is apparent that these rare earth metal nitronyl nitroxide compounds are sources of unusual magnetic behaviors. We therefore decided to extend the investigation to other compounds.

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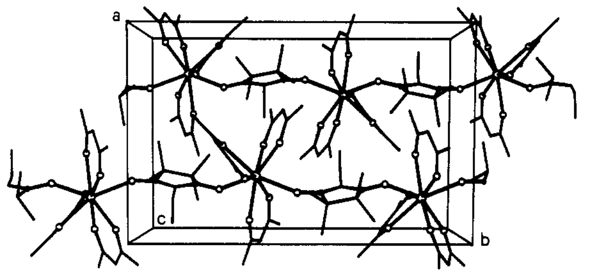

Figure 1. Schematic view of the crystal structure of RE(hfac)$_3$NITEt.

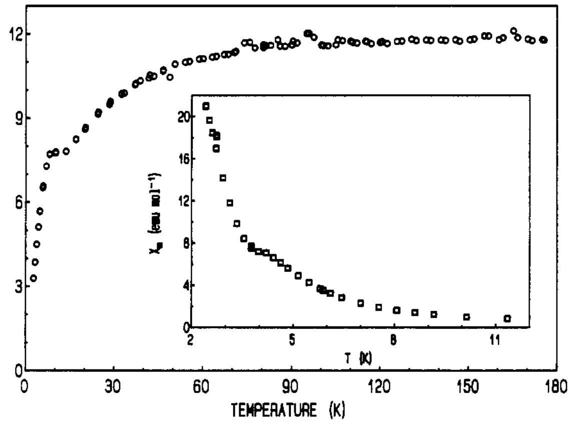

Figure 2. Temperature dependence of the magnetic susceptibility of a powdered sample of Tb(hfac)$_3$NITEt in the χT form measured in a magnetic field of 5 kOe (○). In the inset the susceptibility measured in 200 Oe (□).

In particular we wish to report here the magnetic properties of RE(hfac)$_3$NITEt, (RE = Tb, Ho, and Er), which show magnetic phase transitions at temperatures ranging from 1.2 to 3.2 K, together with an attempt to model the properties of NITR–RE chains.

Experimental Section

Synthesis and Structure of the Compounds. M(hfac)$_3$NITEt, M = Er, Tb, and Ho, were prepared as previously reported for the gadolinium and dysprosium derivatives.[16] X-ray diffraction analysis of suitable single crystals of the new compounds provided monoclinic unit cells very similar to that of Dy(hfac)$_3$NITEt[21] for M = Er (a = 11.23 Å, b = 17.20 Å, c = 18.35 Å, β = 98.2°) and for M = Ho (a = 11.21 Å, b = 17.33 Å, c = 18.32 Å, β = 98.4°). Tb(hfac)$_3$NITEt is instead similar to the gadolinium derivative[14] (a = 20.10 Å, b = 17.08 Å, c = 22.66 Å, β = 113.9°). The compounds are assumed to be isostructural with the dysprosium and gadolinium derivatives respectively. A sketch of the chain structure of the compounds is shown in Figure 1.

Physical Measurements. The single crystals were checked and oriented with a four-circle Enraf-Nonius CAD4 diffractometer. The dc magnetization was measured with a Metronique MS02 SQUID magnetometer operating between 2.2 K and room temperature with the applied magnetic field up to 8 T. Ac susceptibility was measured with a laboratory-assembled susceptometer based on a mutual inductance bridge. Magnetic anisotropy measurements were performed on samples prepared by gluing several single crystals (10–20) on a silicon support.

Results

Magnetic Properties. The temperature dependence of χT for Tb, in an external field of 5000 Oe, is shown in Figure 2. The room-temperature value, 11.8 emu mol^{-1}K, is close to the value expected for uncoupled terbium(III) (11.81 emu mol^{-1} K) plus organic radical (0.375 emu mol^{-1} K), and it steadily decreases with temperature, reaching ca. 3 emu mol^{-1} K at 4 K. In order to avoid saturation effects the measurements were performed also in external fields of 200 Oe, and in the inset of Figure 2 we show that χ vs T plot in the range 2–14 K. The experimental data show a shoulder at ca. 4 K. The ac susceptibility, measured without an applied magnetic field, shows a peak in the in-phase component, χ', at 1.8 K and a peak in the out-of-phase component, χ'', with the maximum at 1.7 K. The temperatures of the peaks do not change on varying the frequency of the measurement.

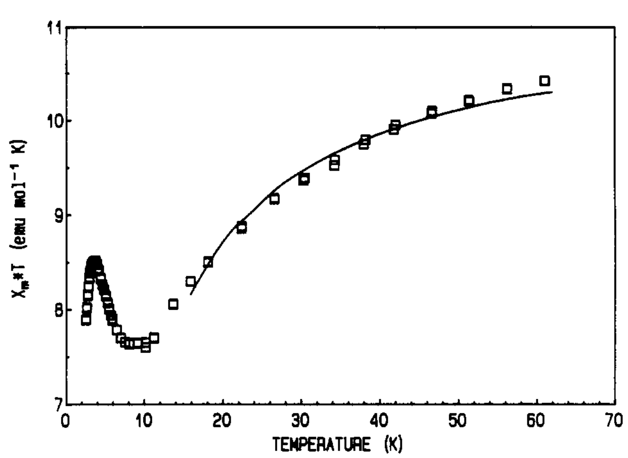

Figure 3. Temperature dependence of the powder magnetic susceptibility of Er(hfac)$_3$NITEt in the χT form measured in a magnetic field of 5 kOe. The solid line represents the best fit with the model described in the text.

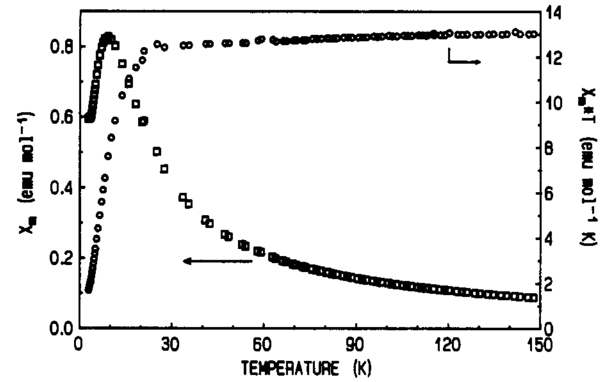

Figure 4. Temperature dependence of the magnetic susceptibility of a microcrystalline sample of Ho(hfac)$_3$NITEt measured in a magnetic field of 5 kOe.

Er(hfac)$_3$NITEt has a room temperature value of χT of 11.0 emu mol^{-1} K, to be compared to the sum of the values expected for uncoupled erbium (11.45 emu mol^{-1} K) and radical (0.375 emu mol^{-1} K). χT decreases steadily, Figure 3, reaching down to ca. 10 K, when it reaches a minimum of 7.6 emu mol^{-1} K at ca. 8 K. Below the minimum, χT increases, reaching a maximum at 3.7 K, corresponding to 8.52 emu mol^{-1} K. Below the maximum, χT decreases to reach 7.90 emu mol^{-1} K at 2.5 K. No maximum is observed in the susceptibility. Ac susceptibility measurements show that the in-phase susceptibility goes through a maximum at 1.2 K, with a shoulder at ca. 1.7 K. The out-of-phase susceptibility is fairly small.

Ho(hfac)$_3$NITEt has χT of ca. 13 emu mol^{-1} K at room temperature, to be compared with the sum of the values expected for holmium (14.05 emu mol^{-1} K) and radical (0.375 emu mol^{-1} K). The temperature dependence of χT shows a monotonic decrease (Figure 4), while χ goes through a maximum at 7 K. The presence of the maximum clearly indicates antiferromagnetic behavior.

Magnetic anisotropy measurements could be performed on single crystals of Ho(hfac)$_3$NITEt. Since the shape of the crystals is that of elongated prisms, good control of the orientation could be achieved for the long direction of the crystals, which corresponds to the chain axis b, while the orientations perpendicular to this direction could not be adequately checked. The reported values can therefore be described as an average in the ac plane. The results are shown in Figure 5. $\chi_\perp$ goes through a maximum at ca 7 K, while $\chi_\parallel$ increases steadily throughout the temperature

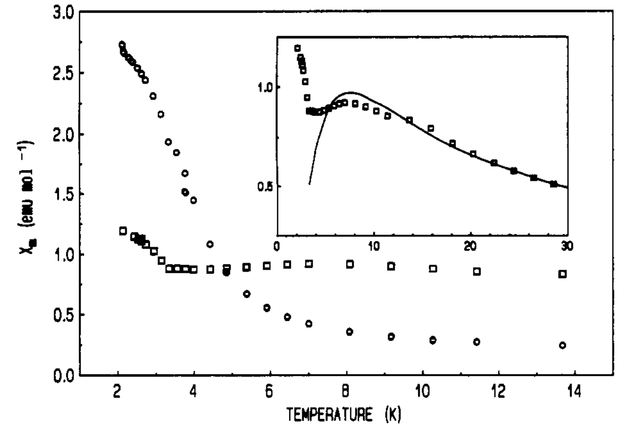

Figure 5. Temperature dependence of the magnetic susceptibility of Ho(hfac)$_3$NITEt measured parallel to *b* (○) and in the *ac* plane (□) with an external field of 200 Oe. The solid line represents the best fit with the model described in the text.

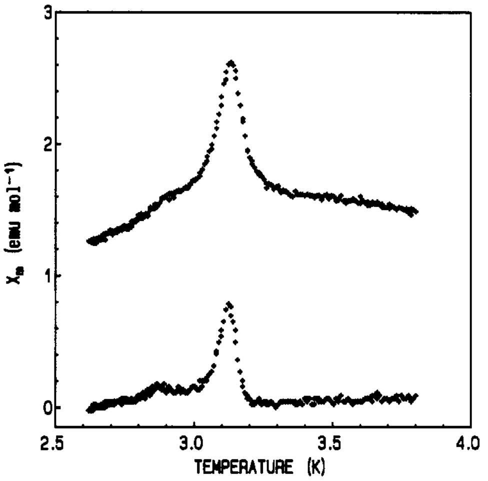

Figure 6. Temperature dependence of the magnetic susceptibility of Ho(hfac)$_3$NITEt measured in zero static field: real part of the ac susceptibility measured at 97 Hz (top); imaginary part of the ac susceptibility (bottom).

interval (the symbols refer to the chain direction). $\chi_\parallel$ is smaller than $\chi_\perp$ in the paramagnetic phase, suggesting that the anisotropy is of the XY type, but at low temperature $\chi_\parallel$ increases much faster than $\chi_\perp$, determining a crossover in the anisotropy at ca. 4.5 K.

The ac susceptibility of a polycrystalline sample without an applied magnetic field at a frequency of 97 Hz in the range 2.5–4 K is shown in Figure 6. χ' has a peak at 3.1 K, with a shoulder at 2.9 K. Analogous behavior is observed for the out-of-phase component χ''.

The single crystal magnetization at 2.3 K is shown in Figure 7. $M_\parallel$ increases rapidly in small fields and then increases slowly, with the indication that saturation is not reached in a field of 70 kOe. The largest observed value is $M_\parallel$ = 16 700 emu G mol^{-1}. $M_\perp$ also increases initially, but after slowing down, for fields larger than 10 kOe it has a second rapid increase and does not saturate in fields up to 70 kOe. The largest value which was achieved corresponds to $M_\perp$ = 39 500 emu G mol^{-1}.

Discussion

The RE(hfac)$_3$NITEt compounds investigated so far and the nature of the ground state of the rare earth metal ions are shown in Table I. There are two relevant points in the magnetic behavior of these compounds which deserve comment: one is the overall antiferromagnetic behavior in the paramagnetic phase; the other is the presence of magnetic phase transitions in all compounds with anisotropic rare earth metal ions. In the following we will address the former point first, suggesting which mechanisms can be efficient in determining the observed behavior.

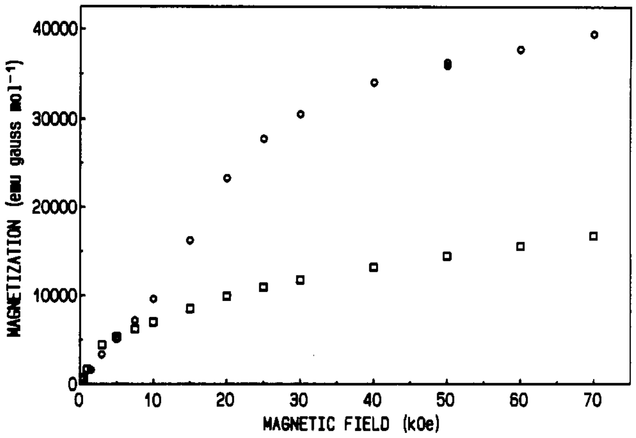

Figure 7. Magnetization curve of Ho(hfac)$_3$NITEt measured parallel to *b* (□) and in the *ac* plane (○) at 2.3 K.

Table I. Magnetic Properties of Rare Earth Metal Nitronyl Nitroxide Chain Compounds

RE	critical temp, K	ground state	g^a	$J_{\text{RE-RE}}{}^b$	$J_{\text{RE-R}}{}^b$	$J_{\text{R-R}}{}^b$
Y		$S = 0$				12
Eu		$^7F_0$				4.5
Gd		$^8S_{7/2}$	2.0	0.7	−1.4	13.5
Tb	1.7	$^7F_6$				
Dy	4.3	$^6H_{15/2}$	13.7	6.8	−0.30	8.1
Ho	3.2	$^5I_8$	8.6	3.5	−2.6	7.7
Er	1.2	$^4I_{15/2}$	10.7	4.7	−0.15	17.5

[a] g values of the rare earth ions estimated by the fitting of the magnetic susceptibility. For Dy and Ho we report $g_\perp$. [b] Coupling constants in cm^{-1}, evaluated by the fitting of the magnetic susceptibility.

The yttrium[15] and europium[14] derivatives strongly point out an efficient mechanism for the antiferromagnetic exchange interaction between the radicals mediated by the metal ions. Yttrium(III) is isoelectronic to bromide, so it can be imagined that the superexchange mechanism involves the 4p doubly occupied orbitals of the metal ion. Therefore, the observed antiferromagnetic coupling can be justified by the admixing of an excited R$^+$–Y^{3+}–R$^-$ state into the ground state. Both R$^+$ and R$^-$ states are relatively easily accessible as shown by the redox behavior of the radicals.[17]

Europium(III) has a nonmagnetic ground state due to the cancellation of spin and orbital components. If we neglect the possible contributions arising from the f orbitals the radical spins can interact through the empty 5d or 6s orbitals of the metal ions. A possible mechanism is depicted in Figure 8a. It corresponds to the admixing of an excited state R$^+$–Eu$_{d,s}{}^{2+}$–R$^\bullet$ into the ground state. Eu$_{d,s}{}^{2+}$ means that the extra electron goes in a d(s), not in an f, orbital.

The antiferromagnetic behavior observed with the magnetic rare earth metal ions suggests the presence of dominant next-nearest-neighbor antiferromagnetic interactions. In fact the alternative explanations of strong antiferromagnetic interchain interactions or strong alternation of the intrachain nearest-neighbor interactions were rejected on the basis of structural and magnetic resonance evidence.

The inclusion of n-n-n antiferromagnetic interactions in a chain leads to spin frustration effects, because a given spin is under the conflicting influences of the nearest and the next-nearest neighbors irrespective of the sign of the interaction between nearest neighbors.[23] Therefore the lowest energy spin alignment will neither have all the spins parallel nor spin alternating up and down, as required by nearest-neighbor interactions. More complex

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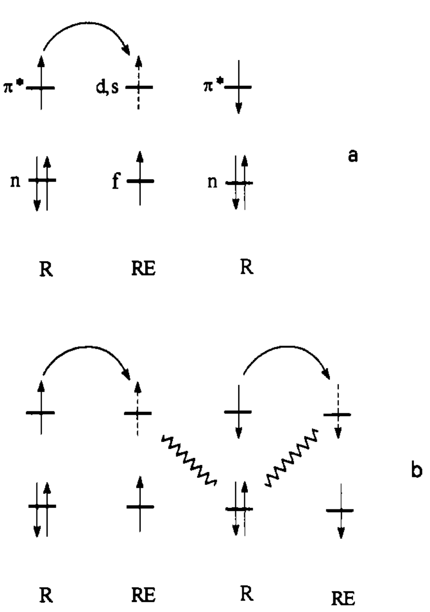

Figure 8. Possible exchange mechanism: (a) a radical–RE–radical group; (b) a radical–RE–radical–RE group including the possibility of a nnn interaction.

spin structures must be expected, along with degeneracy, or quasi degeneracy, of the ground state.

The calculation of the energy levels within a Heisenberg model is by no means difficult,[24] while within an Ising model it can be efficiently tackled with the transfer matrix formalism.[25] An early attempt to use that technique yielded a ground state which can be described as two-spin-up–two-spin-down, corresponding to an $S = 0$ ground state.[16] In the model we worked out, a term was missing. Recently a more accurate calculation was worked out which yielded not only the susceptibility but also the correlation length, either within the two sublattices of gadolinium and radical or between the two sublattices.[26] The experimental susceptibility can be fit with the new model to give $J_{Gd-Gd} = 0.7$ cm^{-1}, $J_{Gd-R} = -1.4$ cm^{-1}, and $J_{R-R} = 13.5$ cm^{-1}, with the hamiltonian defined as $H = J\mathbf{S}_1 \cdot \mathbf{S}_2$. Of course the fit cannot be extended to very low temperature because the Ising model is not expected to be appropriate for gadolinium and radical. However it does show that the experimental data can be at least qualitatively interpreted including nnn interactions. The ground state, which corresponds to a "two-spin-up–two-spin-down" configuration in the Ising limit, should correspond to a helical arrangement of the spins in the Heisenberg limit.

From the above analysis a ferromagnetic interaction between gadolinium and radical and an antiferromagnetic one between gadolinium ions is required. The ferromagnetic interactions between gadolinium and radical are also confirmed by magnetic data of simple compounds containing one gadolinium coupled to one NITR radical.[13] For the ferromagnetic interaction a model has already been suggested which involves the transfer of one electron from the radical into an empty orbital of gadolinium.[15] This fraction of unpaired electron polarizes the unpaired electrons of the inner f orbitals, thus giving rise to a parallel alignment of the spins. The empty orbital was originally suggested by us to be the 6s orbital of the metal ion, while Kahn advocated the 5d orbital.[5] A similar mechanism may be used also for explaining the antiferromagnetic exchange between the metal ions. A rationale for this behavior can be provided by the scheme shown in Figure 8b. The fraction of electron transferred from the left radical into an empty orbital of the left gadolinium ion interacts antiferromagnetically with the fraction of unpaired electron transferred by the right radical onto the right gadolinium ion through a superexchange mechanism involving the lone pair of the radical. Therefore the f electrons of the rare earth metal ions are antiferromagnetically coupled. This means that the excited state which must be admixed into the ground state is R^+–$Gd_{s,d}^{2+}$–R^+–$Gd_{s,d}^{2+}$.

When passing to the anisotropic rare earth metal ions, the exchange interaction must go close to either the Ising or XY limit;[27] it should therefore be expected that the Ising approach should become more appropriate. Applying it to Dy(hfac)$_3$NITEt, which seems to have also XY anisotropy, and assuming that dysprosium(III) can be approximated as an effective $S = {}^1/_2$ with anisotropic g values, yields an acceptable fit of the magnetic susceptibility in the *ac* plane at low temperature with the following parameters: $J_{Dy-Dy} = 6.8$ cm^{-1}, $J_{Dy-R} = -0.30$ cm^{-1}, $J_{R-R} = 8.1$ cm^{-1}, and $g = 13.7$. The value of J_{Dy-Dy} is much larger than J_{Gd-Gd}, but it refers to *effective* spins in the ground state, and therefore it has not an immediate physical meaning.

Holmium(III) has an $^5I_8$ ground state which at low temperature can be treated as a pseudotriplet. Thus assuming an effective spin $S = 1$ for the metal ion the susceptibility in the *ac* plane can be satisfactorily reproduced with the parameters $J_{Ho-Ho} = 3.5$ cm^{-1}, $J_{Ho-R} = -2.6$ cm^{-1}, $J_{R-R} = 7.7$ cm^{-1}, and $g = 8.6$. It is worth noticing that the maximum in the susceptibility is also reproduced as shown in the inset of Figure 5.

Erbium(III) that has a $^4I_{15/2}$ ground state can be treated at low temperature as an effective $S = {}^1/_2$ spin with anisotropic g values as in the case of dysprosium(III). The experimental susceptibility of a powder sample reported in Figure 3 can be nicely reproduced by using $J_{Er-Er} = 4.7$ cm^{-1}, $J_{Er-R} = -0.15$ cm^{-1}, $J_{R-R} = 17.5$ cm^{-1}, and $g = 10.7$.

The most striking feature of this series of compounds is provided by the presence of magnetic phase transitions at relatively high temperatures for the compounds containing anisotropic metal ions. A full understanding of the nature of the magnetically ordered phase requires additional data at low temperature, but the temperature dependence of the magnetic anisotropy of the dysprosium and holmium compounds suggests the presence of weak ferromagnetism. The rapid increase in the susceptibility along the chain direction at T_c can be justified with a misalignment of the antiferromagnetically coupled sublattices, which leads to an uncompensated magnetic moment. If the spins lie essentially in the plane perpendicular to the chain direction, as suggested by the fact that $\chi_\parallel$ is smaller than $\chi_\perp$ in the paramagnetic region, the uncompensated moment arising from the spin canting must be orthogonal to the easy plane, i.e. parallel to *b*. The magnetization curves of Figure 7 are in agreement with this hypothesis. The rapid increase of $M_\parallel$ at low field is consistent with weak ferromagnetism, while the slope of the $M_\perp$ *vs* H curve goes through a maximum at ca. 15 kOe. This metamagnetic behavior is usually observed in antiferromagnet when the interaction of the system with the applied magnetic field becomes the same order of magnitude as the antiferromagnetic interaction.

Several simple salts and hydroxides of the rare earth metal ions ranging from terbium to erbium have been observed to order as bulk ferro- or antiferromagnets in the range of 4 K, but the metal–metal distances in these cases are much shorter than those observed here.[28–31] As an example, the shortest Dy–Dy distance in Dy(OH)$_3$ is 3.53 Å while the corresponding distances in Dy(hfac)$_3$NITEt are 8.74 Å along the chains and 10.76 Å between chains. Generally the magnetic phase transitions in rare earth metal compounds are known to be induced by dipolar interactions,

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but given the long distances between chains in the RE(hfac)$_3$NITEt series, it is not at all obvious how this may be effective, unless strong spin correlation are operative within chains. We exclude the possibility that exchange between chains is relevant. In fact it has been found to be vanishingly small in M(hfac)$_2$NITEt compounds, M = Mn and Cu, which have similar interchain contacts.[32-34] Further, single-crystal EPR spectra of Gd(hfac)$_3$NITR showed marked spin diffusion effects, a clear indication that the ratio of the intra- to the interchain interaction is larger than 10^3.[16] Therefore we must conclude that the intrachain exchange interaction is determinant in order to achieve magnetic order. In fact for the transition metal ions compounds M(hfac)$_2$NITEt, the strong intrachain coupling was found to create such strong correlations within the chains that even the weak dipolar interactions between chains could induce a magnetic phase transition at ca. 8 K.

The fit of the magnetic data in the paramagnetic phase of Dy(hfac)$_3$NITEt suggests $J_{\text{Dy-Dy}} = 6.8$ cm^{-1}. By using for the correlation length, $\xi(T)$, within the dysprosium sublattice the expression[35]

$$\xi_{\text{Dy}}(T) = 2\exp(J/2kT)$$

valid for an Ising chain of $S = {}^1/_2$, it is possible to guess the critical temperature T_c to magnetic order using the available formula which was successfully used for the Mn(hfac)$_2$NITR compounds[36]

$$kT_c = E_{\text{int}}\xi(T_c)$$

where E_{int} is the dipolar energy. In the present case some difficulties arise because the g values are not exactly known but only extrapolated by the single crystals magnetic measurements. Further if the ordered phase is antiferromagnetic several spin structures are possible, but assuming that the ground state of the chains has a "two-spins-up–two-spins-down" configuration we evaluated a dipolar energy $E_{\text{int}} = 0.05$ K and therefore a critical temperature $T_c \approx 2$ K, in good agreement with the experimental data.

According to the above analysis, the unusually high critical temperatures for anisotropic RE(hfac)$_3$NITEt compounds must be essentially determined by the strong antiferromagnetic exchange between the rare earth metal ions mediated through the radical ions. Additional work at very low temperature, including specific heat, is in progress to better characterize these molecular magnets.

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