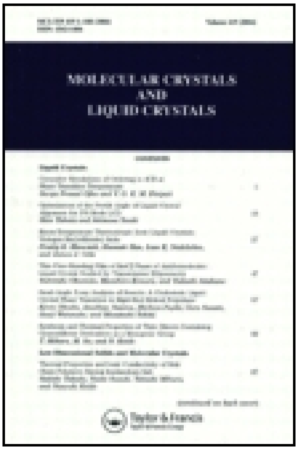

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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MAGNETIC MATERIALS FORMED BY METAL IONS AND NITROXIDES

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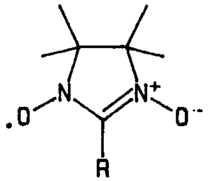
Abstract The metal–radical approach to the synthesis of molecular magnets is reviewed. Several examples of zero– and one–dimensional ferrimagnets containing manganese(II) and nitronyl nitroxides are provided, together with the characterization of their magnetic phase transitions at low temperatures.

INTRODUCTION

There are currently several different approaches to molecular magnets, using organic, metallo–organic and inorganic points of view[1]. We are currently following a strategy to assemble metal ions and nitronyl nitroxides, NITR, of general formula shown below, in low dimensional materials in order to determine the conditions under which bulk magnets can be obtained[2].



The choice of the radicals has been dictated by their ability to bind to two different metal ions, yielding polymeric structures in which the magnetic exchange interaction is efficiently transmitted between metal ions with $S \geq 1/2$.

Manganese–radical species appear to be good candidates to yield high spin species, which eventually undergo transition to three–dimensional magnetic order. This can be obtained if the metal and radical species are connected in a three–dimensional array of relatively strong exchange interactions, or also if the metal ions and the nitroxides can be arranged either in rings or in chains which then interact with lower intensity with each other.The former architecture would be preferable, but up to now no suitable radical was found to yield a three–dimensional structure with metal ions, while a few examples of rings and chains are available. In the following we will show some examples of ferrimagnetic materials and report their transitions to three–dimensional ferromagnetic order.

ZERO–DIMENSIONAL MATERIALS

The best example of ferrimagnetic ring we have available is $[Mn(hfac)_2(NITPh)]_6$ (hfac is hexafluoroacetylacetonate) which has the structure[3] shown in Figure 1.

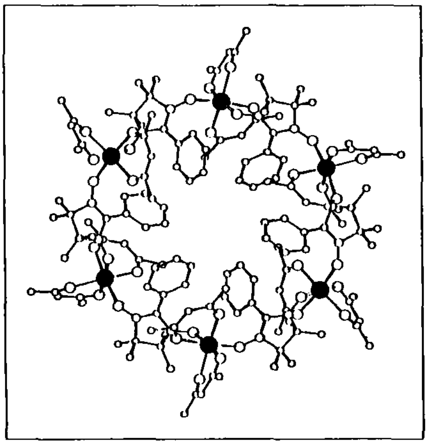


FIGURE 1. Sketch of the structure of $[Mn(hfac)_2(NITPh)]_6$

The manganese ions and the radicals are antiferromagnetically coupled, as shown by the limit value of the effective magnetic moment and by the magnetization at temperatures below 30 K, which clearly indicate a ground S= 12 state. It is interesting to note that down to the lowest temperature which we reached, 2.5 K, the compound remains paramagnetic, thus showing that even if the spin of the cluster is very high the relatively effective shield produced by the bulky hfac molecules prevents the transition to three–dimensional magnetic order.

Therefore it seems that the only possible strategy to build molecular magnets remains that of assembling as intermediate steps at least linear chain compounds, in order to take advantage of the high effective spins which can be established when an infinite number of spins are brought into interaction.

ONE–DIMENSIONAL MATERIALS

Linear chain compounds are formed by manganese hexafluoroacetylacetonates with NITR radicals. We have determined the X–ray crystal structure of $Mn(hfac)_2(NITiPr)$[4], $Mn(hfac)_2(NITEt)$[5], Mn(hfac)(NITnPr)[5], where iPr is *iso*–propyl, Et is ethyl, and nPr is *n*–propyl. The structures of $Mn(hfac)_2(NITiPr)$ and $Mn(hfac)_2(NITEt)$ are shown in Figure 2.

In both cases the manganese ions are bridged by two nitronyl nitroxides and each radical binds to two different metal ions, but in the former the radicals are *trans* to each other in the coordination octahedron, while in the latter they are *cis*. $Mn(hfac)_2(NITnPr)$ has a structure similar to that of $Mn(hfac)_2(NITEt)$. The magnetic properties of both compounds are typical of one dimensional ferrimagnets, with χT diverging at low temperature. The experimental χT values were fitted with a model previously reported for Cu–Mn chains[6], which approximates the S= 5/2 spins with classical spins, while taking into account the quantum nature of the S= 1/2 spins. The best fit values are J= 330 cm^{-1} for $Mn(hfac)_2(NITiPr)$, J= 260 cm^{-1} for $Mn(hfac)_2(NITEt)$, and J= 258 cm^{-1} for Mn(hfac)(NITnPr). Below 20 K for all the complexes the experimental χT curve increases much faster than the calculated one, suggesting that the systems are

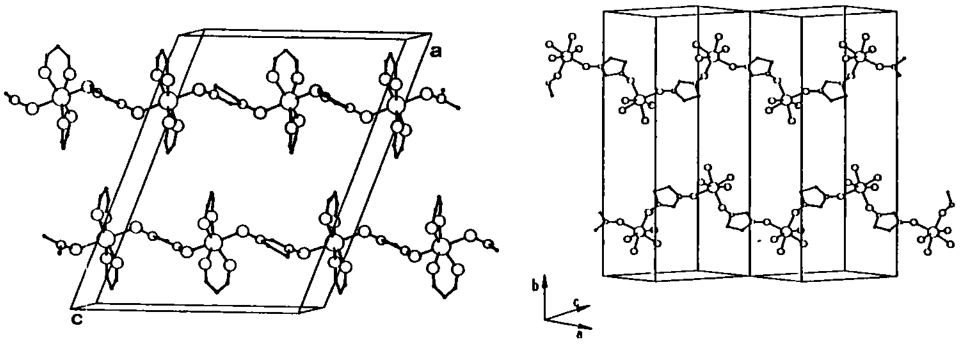


FIGURE 2. Structures of $Mn(hfac)_2(NITiPr)$ (left) and $Mn(hfac)_2(NITEt)$ (right).

approaching the critical temperature corresponding to a magnetic phase transition.

In order to confirm this assumption we performed experiments in low external magnetic fields. The temperatures of the phase transitions thus observed are 7.61 K for $Mn(hfac)_2(NITiPr)$[7], 8.1 K for $Mn(hfac)_2(NITEt)$[5], and 8.6 K for Mn(hfac)(NITnPr)[5], and all of them are ferromagnetic in nature, as shown also by magnetization studies and hysteresis loops. For $Mn(hfac)_2(NITiPr)$ we determined also the critical behavior of the susceptibility, which was found to follow a law:

$$\chi = \Gamma\ (T-T_c)^{\gamma} \tag{1}$$

The critical exponent $\gamma = 1.13$ is closer to the value expected for the axial dipolar ferromagnet ($\gamma \approx 1$) than to the Heisenberg three–dimensional ferromagnet[8] ($\gamma = 1.38$) thus suggesting that the driving force to magnetic order in these compounds is the dipolar interaction between the chains. This experimental result is in line with the structure of the compounds in which the chains are well shielded from each other by the bulky hfac molecules. If the hypothesis of dipolar order is correct, it is possible to calculate approximately the critical temperature with a relation which was found to apply to Heisenberg chains[22]:

$$T_c \cong \xi(T_c)\ |E_{dip}| \tag{2}$$

where $\xi(T_c)$ is the spin correlation length and E_{dip} is the dipolar energy for the lattice. This can be easily calculated within the point dipolar approximation including all the spins around a given central one in a sphere of radius, say, 80 Å, with three different spin orientations. The dipolar energies calculated[7] for $Mn(hfac)_2NITiPr$ are: $E_{\parallel} = 0.26$ K and $E_{\perp} = -0.13$ K, parallel and perpendicular to the chain respectively. For $Mn(hfac)_2NITEt$ we calculate[5] $E_x = -0.15$ K, $E_y = 0.06$ K, $E_z = 0.09$ K, where z is the (101) direction (parallel to the chain), y is the (010) direction and x is orthogonal to them. The results for $Mn(hfac)_2NITnPr$ are practically identical[5] to those of $Mn(hfac)_2NITEt$. The calculated values compare well with the experimental values which we will discuss more at length in the following. The negative values indicate the preferred spin orientation, therefore $Mn(hfac)_2NITiPr$ has a XY type anisotropy, (preferred spin orientation in a plane orthogonal to the chain axis), while both $Mn(hfac)_2NITEt$ and

$Mn(hfac)_2NITnPr$ have an Ising type anisotropy (preferred spin orientation in one direction orthogonal to the chain).

The exact evaluation of the correlation length $\xi(T_c)$ is by no means a simple matter, but an approximate evaluation can be performed through the relation:

$$\xi(T_c) = \frac{\chi(T)}{\chi_c(T)}\frac{S+1}{S} - \frac{1}{S} \qquad (3)$$

where χ is the susceptibility of the chain calculated with the model described above, χ_c is the Curie susceptibility of a system with S = 2. The origin of this formula is that at low temperature each manganese–radical pair is in the ground S = 2 state and the observed susceptibility is determined by the average number of pairs having parallel spins. $\xi(T)$ so calculated indicates that at 20 K the average number of such pairs is 30 for $Mn(hfac)_2NITiPr$.

By substituting the value of $\xi(T)$ evaluated according to (3) in (2), and the dipolar energies calculated above we predict critical temperatures of 8.4–8.8 K for the three compounds of interest, in good agreement with the experimental data, thus giving some confirmation to the hypothesis of a dipolar driving force to three–dimensional magnetic order.

A comment is needed in order to justify why $Mn(hfac)_2NITiPr$, which has the largest value of J has the lowest critical temperature. Our interpretation is that the Ising type anisotropy of the dipolar energy observed for $Mn(hfac)_2NITEt$ and $Mn(hfac)_2NITnPr$ yields a larger $|E_{dip}|$, and therefore a higher transition temperature. Further the correlation length at the critical temperature can also be increased by the Ising type anisotropy, since it is known that $\xi_{Ising} \geq \xi_{XY} \geq \xi_{Heisenberg}$ at a given temperature for the same J value[8].

With the previous considerations we have transferred the problem of the comparison of the critical temperatures for the three compounds to that of justifying why $Mn(hfac)_2NITiPr$ has an XY type magneto–crystalline anisotropy, while $Mn(hfac)_2NITEt$ and $Mn(hfac)_2NITnPr$ have an Ising type.

The experimental determination of the magneto–crystalline anisotropy in the paramagnetic phase was performed by measurements of both single crystal susceptibility and EPR spectra. In fact even at temperatures which are fairly higher than the critical temperatures the spins are ordered at short range due to the strong coupling along the chains and the anisotropy fields give them preferential orientations. These show up in magnetic susceptibility as different values in different crystal orientations, while in an EPR experiment they show up as different shifts of the resonance fields. The two quantities are indeed related because the EPR absorption is the imaginary part of the microwave susceptibility. An explicit relation between the two sets of quantities is given by[9]:

$$B_x = \frac{\sqrt{\chi_y \chi_z}}{\chi_x} \frac{g_e}{g_x} B_0 \tag{4}$$

where x, y, and z are the principal axes of the χ tensor, B_0 and B_x are the free electron and sample resonance fields, g_e and g_x the g factors of the free electron and sample respectively. The resonance fields in the other directions follow from cyclic permutations.

The experimental magnetic anisotropy and g values as a function of susceptibility[7] are shown for Mn(hfac)$_2$NITiPr in Figure 3.

The highest susceptibility is observed orthogonal to the chain direction, while the susceptibility along the chain has the lowest value. Correspondingly the g value parallel to the chain decreases on increasing temperature (the resonance field increases) while orthogonal to the chain the g values increase (the resonance fields decrease). The highest g value is observed parallel to *b*. The g shifts of Mn(hfac)$_2$NITEt on the other hand increase parallel to x, and decrease along the other directions, the smallest value being observed parallel to y[5].

In order to understand the difference of behavior it is necessary to

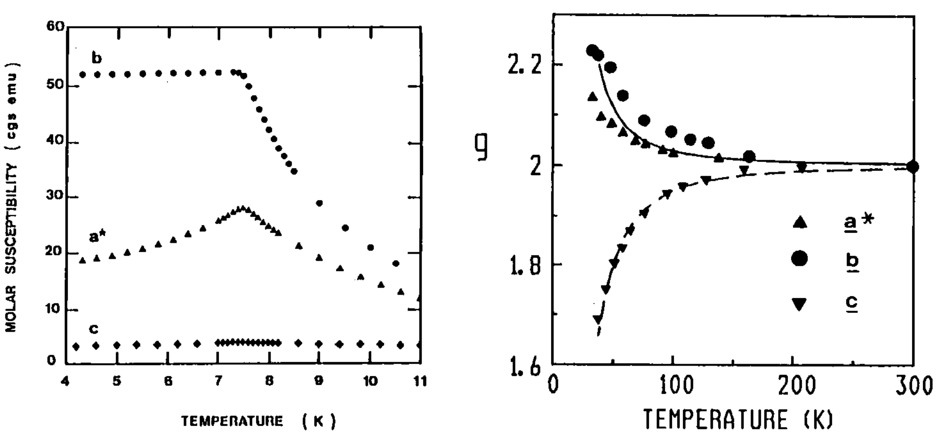


FIGURE 3. Magnetic anisotropy (left) and g shifts (right) of single crystals of Mn(hfac)$_2$NITiPr.

understand which are the factors determining the preferred orientation of the spins in one–dimensional magnetic materials under the influence of anisotropic exchange and dipolar interactions within the chains. For a one–dimensional ferromagnet exchange tells the spins to be parallel to each other, and the dipolar coupling sends the same information, therefore the preferred spin orientation is along the chain, with an Ising type anisotropy. As a consequence the highest susceptibility is along the chain, where the g shift is downfield. This has been experimentally found[10] in the EPR spectra of the one–dimensional ferromagnets $Cu(hfac)_2NITMe$.

On the other hand, antiferromagnetic exchange tells the neighboring spins along the chain to orient antiparallel to each other, while the dipolar interaction tends to keep them parallel. Therefore the preferred spin orientation is orthogonal to the chain. However for a one–dimensional antiferromagnet the plane orthogonal to the chain corresponds to the lowest susceptibility, because the moments are not compensated as shown in Figure 4. As a consequence the resonance fields are expected to have a positive shift along the chain and negative orthogonal to that as we have experimentally observed[7] for $Mn(hfac)_2NITiPr$.

The different behavior of $Mn(hfac)_2NITEt$ and $Mn(hfac)_2NITnPr$ is easily understood in a qualitative way. In fact in these two compounds the chains are *zig–zag* chains rather than straight chains, developing in the yz planes. Therefore the y and z directions become more similar and the preferred spin orientation is along x. A quantitative analysis of the anisotropy data is by no means trivial because it requires the calculation of four–spin correlation functions which can be

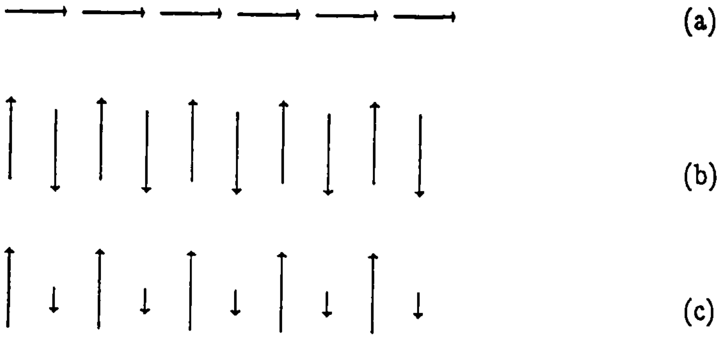


FIGURE 4. Preferred spin orientation for ideal (a) ferromagnets; (b) antiferromagnets; (c) ferrimagnets.

easily calculated only using classical spins[11]. The approximation is not too bad for manganese, but certainly less accurate for the radicals. However the difficulty to use more rigorous approaches makes also this approximation acceptable. Using this approach we developed[7] a formula to calculate the susceptibility and the g shifts for ferro– and ferrimagnetic chains formed by $S_a = 5/2$ and $S_b = 1/2$, and the results are shown in Figure 3. It is apparent that the quantitative results confirm the qualitative predictions above and that sizeable g shifts begin to be clearly observable at relatively high temperatures.

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