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From purely organic to metallo-organic chiral magnetic materials

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Abstract

There is presently a widespread search for materials which present magnetic ordering and appropriate chiroptical properties which would allow the observation of magneto-chiral effects. In this paper, we reflect on the possible uses of organic materials to probe this phenomenon, either as pure compounds or as their coordination compounds with metal ions.

Keywords: Chirality; Circular dichroism; Nitroxide; Manganese

1. Introduction

Since the prediction and especially the experimental observation of magneto-chiral dichroism (MChD) [1–4]—an additional weak effect to natural circular dichroism (NCD) and magnetic circular dichroism (MCD)—a host of research groups involved in the study of molecular magnets [5,6] have embarked on programmes bent on the creation of magnetically ordered optically active materials (that show selective absorption, refraction or emission of light) [7]. It is hoped that the massive internal magnetic field of these materials will give rise to large MChD effects. Chiral magnetic materials have been prepared deliberately with these phenomena in mind [8–17], coincidentally [18–23], or with other objectives in sight [24–28].

Chirality in any material may result from the presence of atomic stereogenic centres, as is most commonly seen in organic compounds and their complexes [29], or atropoisomeric conformations (which interconvert more or less slowly), as typified by some transition metal complexes. Alternatively, an achiral molecule may be frozen into a chiral conformation when it condenses in the solid state, and in the case that spontaneous resolution occurs enantiomorphous crystals can be formed [30,31]. This situation has been observed in a number of purely organic nitronyl nitroxides [32–35] as well as is the case of a manganese(II)bis-hexafluoroacetylacetonate complexes of an achiral phenyl nitronyl nitroxide [18,20] or ferrocenyl-bis(nitronyl nitroxide) [23] (Fig. 1).

With all these results in mind, we reflect here on our own foray into chiral magnetic materials, which started out being limited to purely organic nitronyl nitroxides [8,11,13,36], but has more recently turned to their coordination compounds, for reasons that will become clear along the length of the article.

2. Results and discussion

The desire to incorporate a stereogenic centre into the substituents of phenyl nitronyl nitroxides led to the preparation of a number of chiral compounds (Fig. 2), in both enantiomerically pure as well as racemic forms, which have a gross chiral conformation, as observed in X-ray crystallographic studies on single crystals [37].

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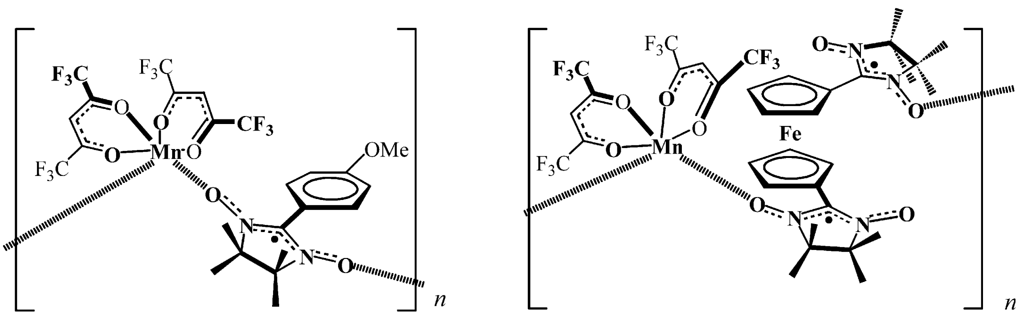


Fig. 1. Radical-Mn(hfac)$_2$ complexes which resolve spontaneously.

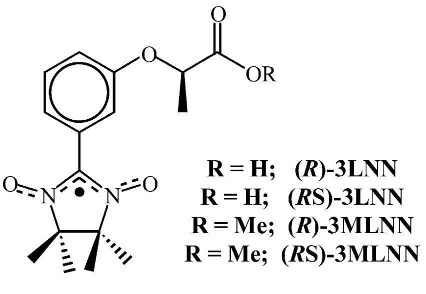
The chiral nature of the compound can affect dramatically the dimensionality—and as a consequence magnetic properties—of these compounds. For example, the enantiopure (*R*)-**4LNN** crystallises as a hydrogen-bonded chains of molecules, while the racemic compound exists as a cyclic dimer in which the two enantiomers are connected head-to-tail by the same type of [C–O–H···O–N] hydrogen bonds as in the former (Fig. 3) [38].

All the enantiopure compounds in Fig. 2 show optical activity, as witnessed in their circular dichroism spectra in the solid as well as solution states. The nature of the spectra in the dynamic (solution) and static (solid) situations is very different, for the reason that in the solution state many of the low-lying conformations are populated, which depend on the solvent–solute interactions [39], while in the solid state a conformation determined by intermolecular interactions and crystal packing restrictions.

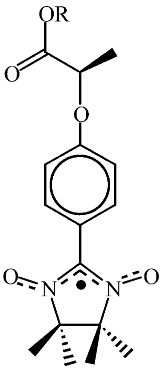
We were interested in trying to observe MChD effects in these purely organic materials. Since none of the chiral materials prepared by us up to now present magnetic order, we tried to determine an MChD effect in solution, but none could be found. The magnitude of the MChD effect is roughly equal to the product of the asymmetry factor (g) of the NCD ($g_{\mathrm{NCD}} = 2(\varepsilon_{\mathrm{L}} - \varepsilon_{\mathrm{R}})/(\varepsilon_{\mathrm{L}} + \varepsilon_{\mathrm{R}}) = 2\Delta\varepsilon/\varepsilon$) and that of MCD effects ($g_{\mathrm{MCD}} = 2[(\varepsilon_{\mathrm{L}\rightarrow} - \varepsilon_{\mathrm{R}\rightarrow})/(\varepsilon_{\mathrm{L}\rightarrow} + \varepsilon_{\mathrm{R}\rightarrow})]B$ where B indicates the magnetic field and the arrows its direction with respect to the incident light beam) [2].

All the organic radicals we have studied present large absorption in the visible region of the electromagnetic spectrum, and the Cotton effects are located in the areas of these absorptions, a situation which results in low asymmetry factor values (Table 1). On top of that the MCD spectra of the radicals show extremely weak effects, as can be appreciated for the radical (*R*)-**3LNN** in Fig. 4. Thus, the value of g_{MChD} is so small as to negate the observation of the MChD effect in these organic compounds. It should be pointed out that in the Europium complex in which MChD was observed, the high anisotropy of the metal ion combined with the disallowed nature of the probe transition conspired to give a g_{MChD} of sufficient magnitude to make possible the measurement in emission [1].

The complex formation between nitronyl nitroxides and metal hexafluoroacetylacetonates [M(hfac)$_2$] [40–43] is an excellent way to try and generate materials with magnetic ordering and sizeable magnetic anisotropy as well as varied optical activity with respect to the component parts as a result of the metal-to-nitroxide interaction. For this reason, we attempted the formation of Mn(hfac)$_2$ and Co(hfac)$_2$ complexes of all the non-acid nitronyl nitroxides present in Fig. 2. Of all the crystallisation attempts with racemic and enantiomeric material, only one has produced satisfactory crystals up to now: that of (*R*)-**3MLNN** [16]. The complex formed between (*R*)-**3MLNN** and Mn(hfac)$_2$ crystallises in such a way that the two components form a polymeric chain comprised of a 2_1 chain (not a helix) (Fig. 5). Each



R = H; (*R*)-3LNN
R = H; (*RS*)-3LNN
R = Me; (*R*)-3MLNN
R = Me; (*RS*)-3MLNN



R = H; (*R*)-4LNN
R = H; (*RS*)-4LNN
R = Me; (*R*)-4MLNN
R = Me; (*RS*)-4MLNN

Fig. 2. Chiral phenyl nitronyl nitroxides prepared up to now.

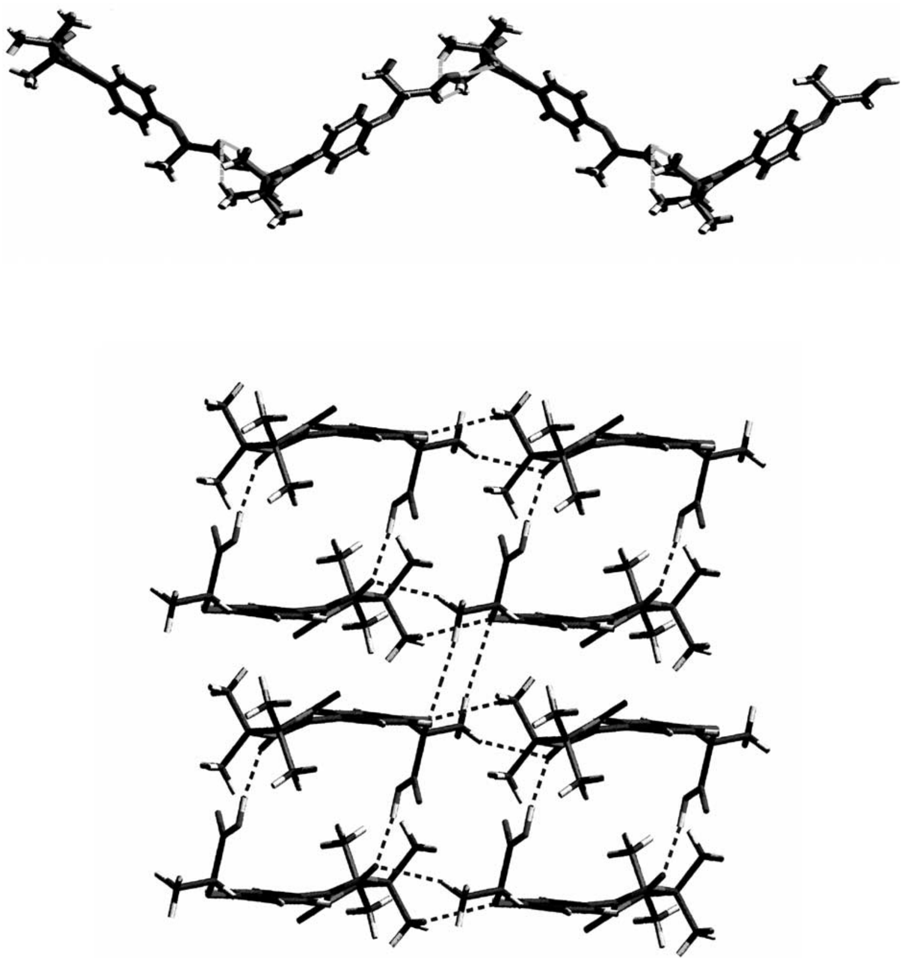


Fig. 3. Crystal packing of (*R*)-**4LNN** (above) and (*R*,*S*)-**4LNN** (below).

oxygen atom of the ONCNO unit of the radical coordinate to the paramagnetic metal ion in a *cis* manner. The stereogenic centre in the organic radical, located very far away from the coordination site, induces a chiral Λ configuration, or minus (*M*) helicity, of the metal coordination sphere. This kind of passage of stereochemical information is common in coordination chemistry [44], although its passage over such a large distance is less well documented perhaps because of its contra-intuitive nature. It is perhaps the molecular conformation of the radical component in the complex that is responsible for this passage of chiral information, since it is very similar to the pseudo-eclipsed one present in crystals of the pure organic ligand, which crystallises in the same chiral space group ($P2_12_12_1$) as the complex.

Table 1
Calculated g_{NCD} values in solution and solid states for a series of organic radicals prepared in our work (Fig. 2)

Compound	Solution (CH_2Cl_2)			Solid (KBr)	
	360 nm	430 nm	600 nm	360 nm	480 nm
(*R*)-**3LNN**	1×10^{-4}	4×10^{-3}	1×10^{-4}	6×10^{-4}	4×10^{-4}
(*R*)-**3MLNN**	1×10^{-4}	6×10^{-3}	2×10^{-4}	2×10^{-3}	1×10^{-3}
(*R*)-**4LNN**	1×10^{-6}	1×10^{-4}	1×10^{-4}	1×10^{-3}	8×10^{-4}

The chains pack parallel to each other such that each one is surrounded by six neighbours some of which are related by a screw-axis (Fig. 6). The shortest inter-chain distances are from fluorine atoms of the CF_3 groups and

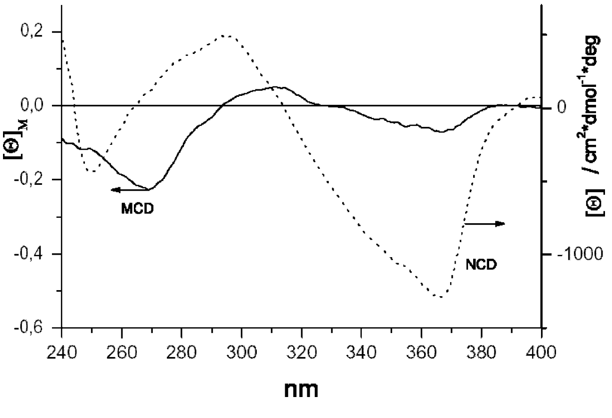


Fig. 4. The NCD (dashed line) and MCD (solid line) spectra of (*R*)-**3LNN** in dichloromethane at room temperature.

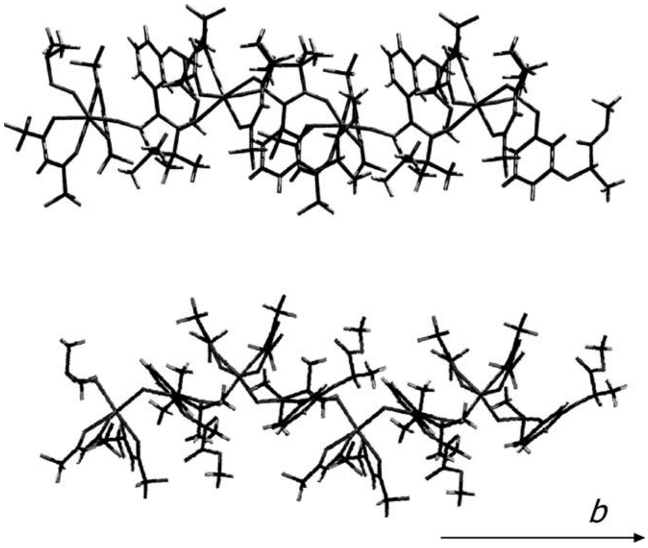


Fig. 5. Views of the coordination polymer chain of (*R*)-**3MLNN**·Mn(hfac)$_2$.

CH groups from the two ligands (the nearest inter-chain metal ion to metal ion distances range from 11.33 to 12.54 Å).

The UV–visible absorption spectra of the complex in KBr matrix shows a longer wavelength visible absorption than the pure radical, a shift in the absorption is mirrored by changes in the optical activity of the complex. The circular dichroism (CD) spectra of the ground crystals, also in KBr matrix, a technique we have paid special attention to developing [13], showed that the complex has Cotton effects that are as intense as those of the radical, and in particular has one, at approximately 460 nm (Fig. 7), which is very interesting for the possible observation of magneto-chiral effects. The reason is that the natural CD asymmetry factor ($g_{\mathrm{NCD}} = 2(\varepsilon_- - \varepsilon_+)/(\varepsilon_- + \varepsilon_+) = \Delta\varepsilon/\varepsilon$) is higher in the complex than in the ligand, and in addition the metal complex orders magnetically.

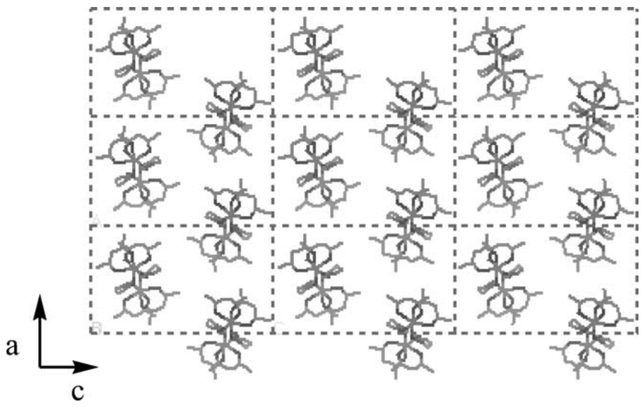


Fig. 6. View of the packing of the coordination polymer chain of (*R*)-**3MLNN**·Mn(hfac)$_2$ seen down the chain axis.

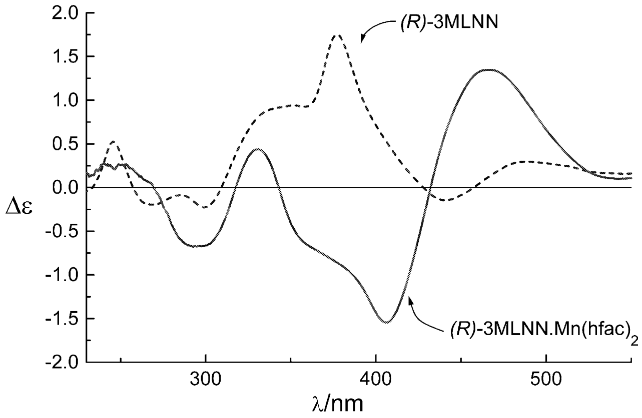


Fig. 7. Solid-state CD spectra of complex (*R*)-**3MLNN**·Mn(hfac)$_2$ and the component radical.

It is perhaps not obvious that while in the crystal the (*R*) configuration correlates with an *M* helicity (Λ configuration), the possibility of a *P* helicity is evidently less thermodynamically favourable. This combination of (*R*) configuration and *P* helicity is a diastereomer of the observed compound, and as such would present different chiroptical properties (CD spectrum), melting point, IR spectrum and so on. To rule out this unlikely possibility, we recorded the CD spectra of several ground single crystals, and upon a larger sample of ground crystals: all the spectra were identical.

The magnetic susceptibility behaviour of a ground sample of the complex (*R*)-**3MLNN**·Mn(hfac)$_2$ exhibits a continuous increase of $\chi_m T$ when the sample is cooled down, going from a value $\chi_m T = 5.6$ cm^3 K mol^{-1} at 350 K, and reaching very high values at low temperatures before reaching a maximum at approximately 3 K and finally decreasing (Fig. 8).

This is a behaviour characteristic of other Mn(hfac)$_2$-nitronyl nitroxide complexes, which act as one-dimensional Heisenberg ferrimagnets, since the isotropic spins of the Mn$^{\mathrm{II}}$ ion ($S = 5/2$) and of the radical ($S = 1/2$) do not compensate and give an escalating magnetic moment as the correlation length increases when the temperature is lowered. The experimental data above 50 K was described adequately by the Seiden model [45,46]. The J value (exchange coupling between $S = 1/2$ and 5/2 units) extracted from this adjustment was 105 cm^{-1} with a fixed $g = 2$ value ($H = -2JS_1S_2$), of the order of previous ones found in this type of complex [18,20,40]. The maximum of $\chi_m T$ at low temperatures indicates that the already correlated spins within each chain order magnetically between each other. This hypothesis was confirmed by performing a.c. susceptibility measurements, which show a large peak in the real part of the susceptibility and a smaller peak in the imaginary part at around 2.86 K. A second peak is also seen in the out-of-phase signal at even lower temperatures—between 0.6 and 1 K—which shows

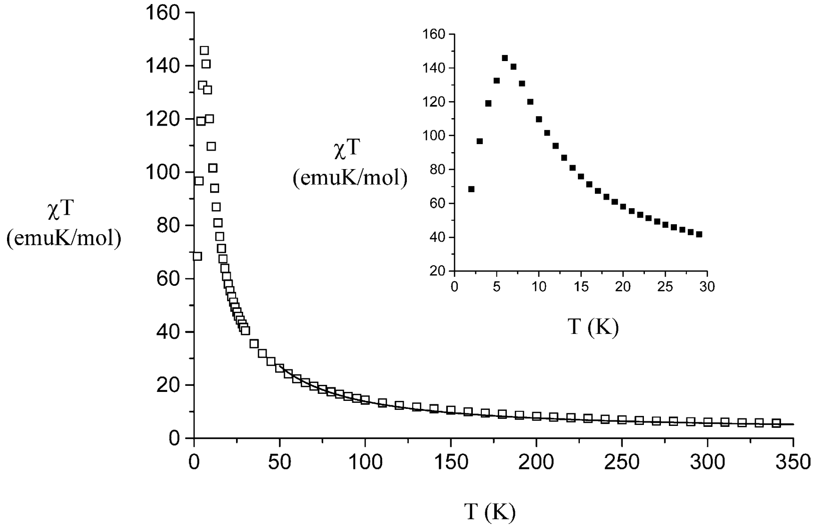


Fig. 8. Magnetic susceptibility (χT plot) of a ground crystalline sample of (*R*)-**3MLNN**·Mn(hfac)$_2$. The solid line is a fit of the data (square points) to the Seiden model.

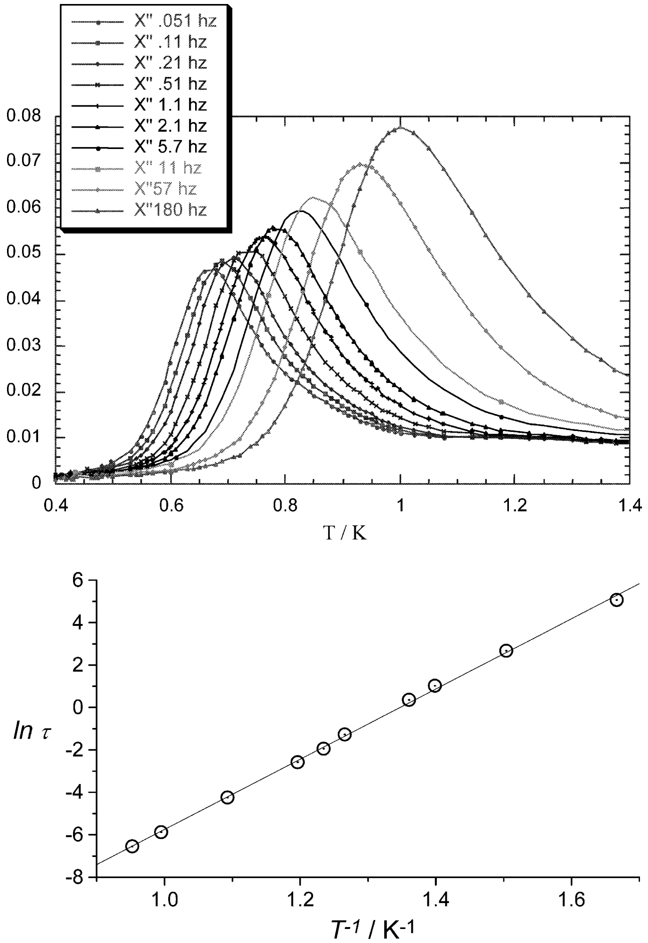


Fig. 9. The frequency dependence of the out-of-phase signal observed at and below 1 K in the a.c. susceptibility measurements of an oriented sample of (*R*)-**3MLNN**·Mn(hfac)$_2$ and an Arrhenius plot showing the thermal activation corresponding to the phenomenon.

frequency dependence with a thermal activation of around 16 K (Fig. 9) [16] (an uncommon occurrence in molecular materials) which is likely to be due to domain wall pinning and depinning in this case, and which is under further intensive study. When these processes are frozen out, hysteretic loops open up, until at 135 mK a magnetic avalanche is clearly observed [16], a rare process, but one seen before in manganese clusters [47,48].

3. Conclusions

Organic radicals are not suitable for the observation of MChD effects, while their metal complexes do hold some promise in this regard. Chirality can have unexpected effects in the preparation of magnetic molecular materials. We are presently exploring the possibilities of this kind of effect in the coordination polymer described here and in other related complexes of homo- and hetero-chiral character.

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