

Pressure Effect on the 3-D Magnetic Ordering of a Quasi-1-D Enantiopure Molecular Magnet

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Magnetic measurements of the quasi 1-D molecular magnet formed by the coordination polymer of purely organic α -nitronyl nitroxide radical and manganese(II) ions, namely [(*R*)-3MLNN–Mn(hfac)₂], have been carried out under pressure up to 10 kbar at low temperatures. The results obtained show that the temperature of 3-D ferromagnetic ordering of the 1-D ferrimagnetic chains in this molecular magnet increases substantially under pressure. Analysis of the experimental data obtained, as well as a review of the ferromagnetic ordering temperature with respect to interchain coupling distances in closely related compounds, gives one grounds to suggest that the interchain magnetic coupling in the 3-D ferromagnetic ordering for this series of coordination complexes cannot be only dipolar (as often inferred). Rather, the interaction must be stronger, and in all likelihood, it is mediated mainly by exchange interactions.

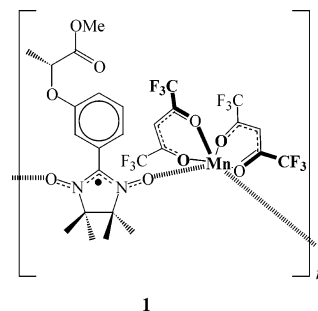
Introduction

Interest in the properties of molecular magnetic materials has resulted in dramatic progress in this area over the last couple of decades.^{1–4} Essentially all of the common magnetic phenomena associated with conventional transition metals and rare-earth-based magnets can be found in molecular-based materials. However, a major advantage of molecule-based magnets is their production by means of controllable molecular chemistry, which allows fine-tuning of structures and magnetic behaviors.^{5,6} Thus, it is possible to modulate structural parameters in order to elucidate the important factors governing otherwise complex behavior. Quasi-one-dimensional (1-D) metallo-organic magnetic systems are a prominent example of this ability to vary properties over broad range.^{7,8} Many of these quasi-1-D complexes order magnetically in three dimensions (3-D) at low temperatures, and it has been argued that this results from ferromagnetic interactions between the 1-D spin chains.^{9–12} However, the mechanistic rationale for this ordering remains, still, somewhat enigmatic.¹³ Understanding the nature of the magnetic interactions in molecular systems constitutes a fundamental step in the development of new molecular magnets with higher magnetic ordering temperatures (T_C).

A prime example of the 3-D magnetic ordering phenomenon is that of the coordination polymers formed by α -nitronyl nitroxides and manganese(II) bis(hexafluoroacetylacetonate), [Mn(hfac)₂]. In these materials, the antiferromagnetically coupled spin $1/2$ of the radical and spin $5/2$ of the metal ion lead to 1-D ferrimagnetic chains with a remnant spin of 2 per repeat unit.¹⁴ The interchain interactions leading to bulk ordering were

originally thought to arise from dipolar interactions because of the relatively large magnetic moment at low temperature, as well as the lack of obvious interchain close contacts and superexchange pathway. However, calculations of dipolar interactions in combination with EPR and SQUID measurements showed that the dipolar interaction alone cannot explain the type of magnetic order exhibited by compounds of this series.¹⁵ Instead, single-ion anisotropies were appealed to as a possible origin of the ordering phenomenon, suggesting strong enough nearest-neighbor-exchange interactions.¹⁵ Hence, the problem of the ordering phenomena in this family of compounds seems somewhat more profound than might be assumed. Being able to describe the nature of this interaction would constitute a major step forward in the understanding of these materials and the design of new molecular magnets.

Recently,¹⁶ we reported the preparation, crystal structure, and optical and magnetic properties of a new coordination compound comprised of one of the purely organic chiral α -nitronyl nitroxides,^{17,18} namely (*R*)-3MLNN, and manganese(II) bis(hexafluoroacetylacetonate), [Mn(hfac)₂]. This crystalline enantiopure chiral complex, (*R*)-3MLNN–Mn(hfac)₂ (**1**) has homo-



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chirality as well as a ferromagnetic phase transition at $T_C = 3$ K. Below T_C , at fields larger than around 10 kOe, the magnetization

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eventually saturates—without any measurable differential susceptibility—at a value of approximately $4\mu_B$, confirming the antiferromagnetic coupling between metal ion and radical spins along the polymeric chains as well as a ferromagnetic alignment of the chains. Upon further cooling, intriguing dynamic behavior was observed, which culminated in the opening up of hysteretic loops below 0.8 K, which were explained in terms of a ferromagnetic domain wall motion. Moreover, a magnetic avalanche phenomenon was found to be below 0.3 K.

In common with other α -nitronyl nitroxide—Mn(hfac)₂ coordination polymers,^{14,15,19–21} compound **1** behaves as a 1-D Heisenberg ferrimagnet with an intrachain antiferromagnetic coupling between the spins of radical and metal ion of approximately 210 cm^{-1} , giving rise to a large net moment at low temperatures.²² Ferromagnetic interactions between these 1-D ferrimagnetic chains leads to 3-D ferromagnetic ordering at the transition temperature $T_C \approx 3\text{ K}$.

In the work described here, we concentrated on the effect of pressure on the ferromagnetic phase transition temperature (T_C) in this molecular magnet (*R*)-3MLNN—Mn(hfac)₂ (see **1**), and have found that T_C increases with increasing pressure. From analysis of the data obtained and a review of the ferromagnetic ordering temperature with respect to interchain coupling distances in closely related compounds, we suggest that the interchain magnetic coupling, which is responsible for the 3-D ferromagnetic ordering for this series of coordination complexes, cannot be only dipolar (as often inferred). Rather, the interaction must be stronger, and most likely is mediated mainly by exchange interactions.

Experimental Section

Compound **1** was prepared according to the previously reported method.¹⁶ Magnetic measurements were done on crystalline samples of the complex **1**. At ambient pressure dc magnetic field properties were measured by using a commercial SQUID magnetometer (Quantum Design) and extraction magnetometry (PPMS); ac susceptibility was also measured in a PPMS system. Pressure-dependent ac susceptibility measurements were performed under quasi-hydrostatic pressure by using a clamp-type piston-cylinder cell adapted for PPMS (Quantum Design) experimental setup, with an organic liquid as pressure-transmitting medium, and taking into account the decrease of pressure when cooling. No diamagnetic corrections have been made. The ferromagnetic signal measured largely overcomes a roughly temperature independent—and small—diamagnetic signal.

Results

In this paper, we first show that the appearance of the 3-D ferromagnetic ordering at low temperatures in the system is signaled by the strong increase of the dc susceptibility, $\chi_{ZFC}(T)$, as well as by the peak in the temperature dependence of the real part of the ac susceptibility, $\chi'(T)$. The existence of hysteretic losses is evidenced by a peak in the out-of-phase component of the ac susceptibility, $\chi''(T)$, (Figure 1). In agreement with previous results,¹⁶ the 3-D long-range ferromagnetic ordering in the compound **1** at ambient pressure is established at $T_C \approx 3\text{ K}$, as defined by the peak position in the $\chi'(T)$ dependence (see Figure 1 and ref 16).

We found that T_C , at which the 3-D ferromagnetic ordering takes place, increases under applying a small dc magnetic field. In Figure 2a, the dc susceptibility, $\chi_{FC}(T)$, and the real part of the ac susceptibility, $\chi'(T)$, which were obtained under the dc field bias of $H = 240\text{ Oe}$, are shown. It can be appreciated that

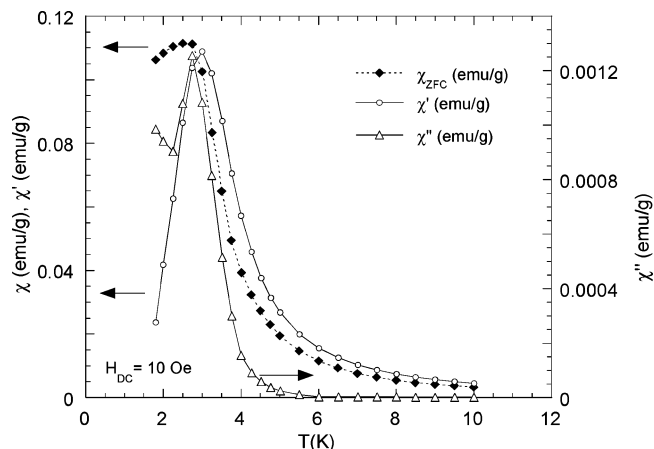


Figure 1. Temperature dependence of the susceptibility of **1** after a zero field cooling process, $\chi_{ZFC}(T)$, in a dc field of 10 Oe. The real, $\chi'(T)$, and the imaginary, $\chi''(T)$, parts of the ac susceptibility as a function of temperature, obtained with an ac field of 5 Oe and 10 kHz frequency, are also shown to make evident the coincidence of T_C with the peak of the $\chi'(T)$ dependence.

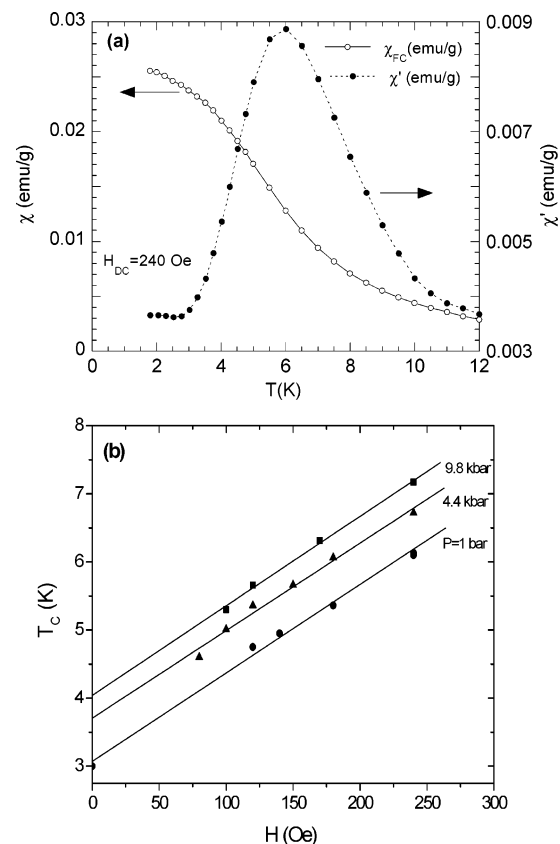


Figure 2. (a) Temperature dependence of the dc susceptibility, $\chi_{FC}(T)$, and the real part of the ac susceptibility, $\chi'(T)$, obtained under the dc field of 240 Oe. (b) The dc field dependence of the 3-D ferromagnetic ordering temperature, T_C , at several applied pressures.

the peak of $\chi'(T)$ is shifted to higher temperature, signaling that the temperature of ferromagnetic ordering actually increases from $T_C \approx 3\text{ K}$ at zero dc field to $T_C \approx 6\text{ K}$ at $H = 240\text{ Oe}$ (compare Figures 1 and 2a). In Figure 2b, we have collected the values of T_C —defined as the maximum of $\chi'(T)$ —as a function of the applied dc field. This figure shows that, in the explored field range ($H < 300\text{ Oe}$), the T_C increases with the rate $dT_C/dH_{dc} \approx (13 \pm 0.3)\text{ K/kOe}$.

The effect of the quasi-hydrostatic external applied pressure (P) on the appearance of the 3-D long-range ferromagnetic

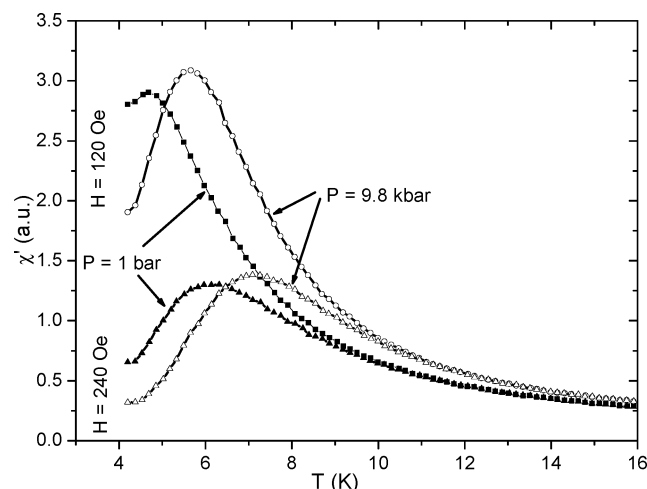


Figure 3. Temperature dependence of the real part of the ac susceptibility, $\chi'(T)$, at ambient pressure (full symbols) and 9.8 kbar (open symbols) for different applied dc fields.

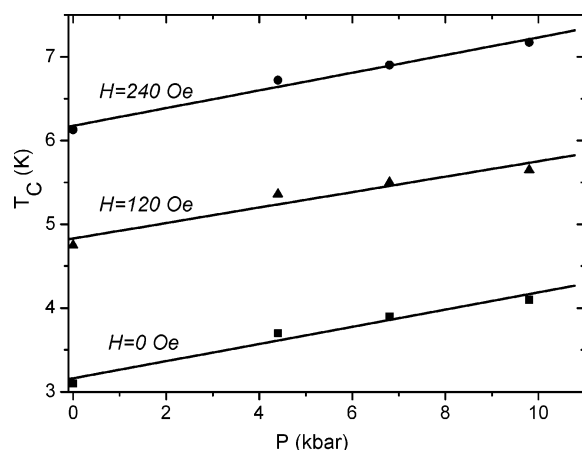


Figure 4. Pressure dependence of the 3-D ferromagnetic ordering temperature (T_C) at different dc magnetic fields.

ordering is displayed in Figure 3. Here we show plots of the real part of the ac susceptibility (χ') vs temperature at ambient pressure ($P = 1$ bar) and $P = 9.8$ kbar obtained at two different H_{DC} bias fields (120 and 240 Oe). An increase of T_C is evidently observed when external quasi-hydrostatic pressure is applied. Thus, ferromagnetic ordering between chains is reinforced upon compression. For example, in a small applied dc field of 120 Oe the peak, observed in the $\chi'(T)$ dependence, reveals $T_C \approx 4.7$ K at 1 bar, while under a pressure of 9.8 kbar the maximum of $\chi'(T)$ is shifted to $T_C \approx 5.7$ K.

The variation of T_C as a function of pressure, measured in several dc fields, is shown in the Figure 4. It is found that the $d(T_C)/dP$ value is practically independent of the applied dc field value, being roughly 0.10 K/kbar in the low magnetic field regime ($H < 300$ Oe). To avoid some uncertainty related to possible nonlinearity of the $T_C(P)$ behavior in the low-pressure range ($P < 3$ kbar), we have also evaluated a slope of the linear part of the $T_C(P)$ dependence in higher pressure range ($3 < P < 10$ kbar), in which the $d(T_C)/dP$ value is around 0.08 K/kbar (in zero field) and gives the corresponding value $(d(\ln T_C)/dP) \approx 0.019$ kbar $^{-1}$.

Discussion

In the discussion, which follows, we will analyze the significance of the pressure dependence of T_C obtained in the experiments reported here. For a quasi-1-D half-integer, anti-ferromagnetically coupled and fully compensated spin system,

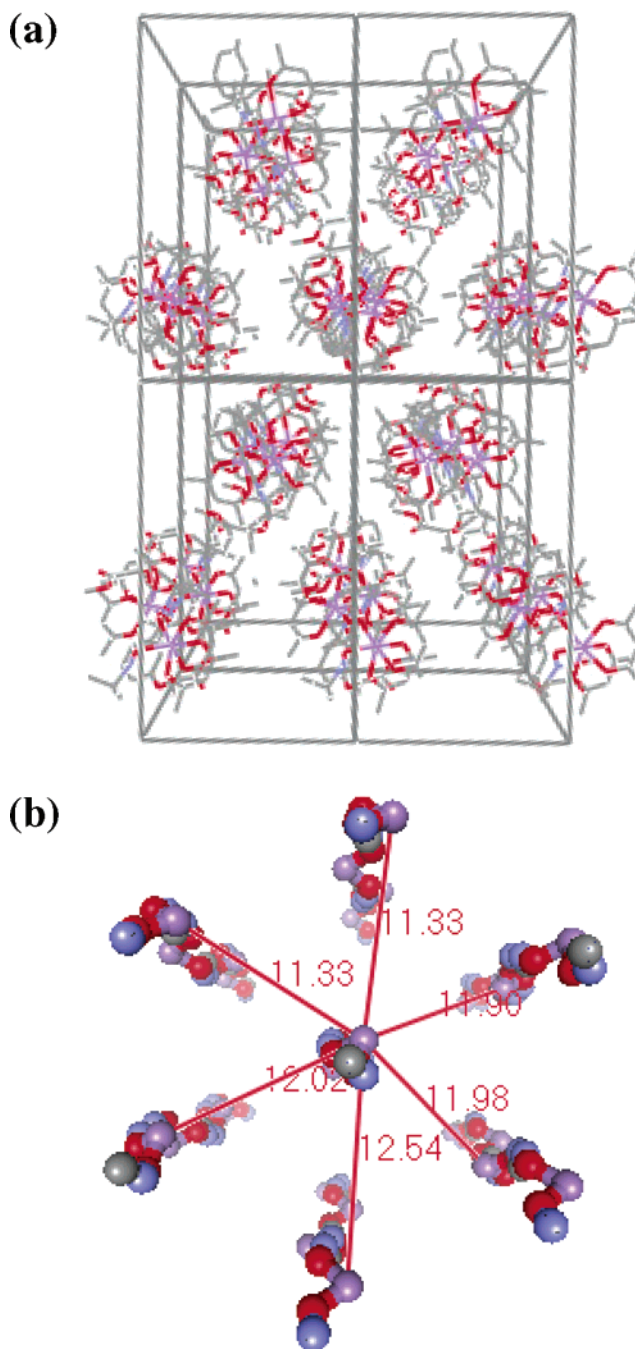


Figure 5. (a) Perspective view for packing of the chains in the crystal structure of **1** with the organic fragments (less H and F atoms) present. (b) Perspective view of the nearest neighboring chains in compound **1**, in which only the $[\text{Mn}-\text{ONCNO}-]$ backbone of the chain is shown. Numbers indicate the six closest Mn-Mn distances between surrounding chains.

a Heisenberg mean field model for the 3D magnetic ordering temperature predicts (to a first approximation) $T_C \propto J_{\perp}$, where J_{\perp} stands for the interchain coupling interaction.^{23,24} More elaborated models lead to second order corrections (i.e., logarithmic),^{23–25} which do not substantially affect the main trend observed here and consequently, we will assume them to be negligible in the following. Notice that the present situation differs from that commonly considered^{23–25} in the sense that the spin chain system is not fully compensated. Even so, in the simplest approximation, we shall take $T_C \propto \sum_i J_i$, where i is the number of nearest-neighbor chains in transverse direction (for the complex studied, $i = 6$, see Figure 5).¹⁶

On the other hand, magnetic interactions are known to be strongly dependent on the coupling bridge length (l_i) between the nearest chains, typically as $J_i \propto k_i(1/l_i)^n$, where the k_i is a parameter corresponding to the strength of the coupling and the exponent n depends on the type of the magnetic interaction (dipolar, exchange, etc.). Therefore, we can write $T_C \propto \sum_i k_i(1/l_i)^n$. Assuming (for simplicity) that $k_i \approx k$ and using the averaged interchain coupling bridge length $\langle l \rangle$, then $T_C \propto (1/\langle l \rangle)^n$. Thus, pressure should promote a T_C change given by

$$\frac{d(\ln T_C)}{dP} = -\frac{n}{\langle l \rangle} \frac{d\langle l \rangle}{dP} \quad (1)$$

To use eq 1 to get an evaluation of the exponent n , which should be indicative of the type of the interchain magnetic interaction, an estimate of the compressibility modulus $\alpha = (1/\langle l \rangle)(d\langle l \rangle/dP)$ in the direction perpendicular to the chains is required. It is worth mentioning here that the compression between chains is expected to be much higher than that along the chains, since in the former there are no strong chemical interactions, while the length of the chain is joined by covalent and coordination bonds (Figure 5). Therefore, quasi-hydrostatic pressure should mainly affect interchain interactions. Unfortunately, we are not aware of any compressibility studies under high pressure for this family of metallo-organic molecular magnetic materials. To get a rough estimate, we can use the compressibility modulus measured in other quasi-1-D organic compounds. In this regard, the quasi-1-D organic salts, (TSeT)₂Cl and (TMTSF)₂ClO₄, are very appropriate as they have been particularly well studied even at $T < 10$ K. According to D. Le Pevelen et al., it turns out that, in the same pressure range as in our experiments, $\alpha \approx -1.64 \times 10^{-3} \text{ kbar}^{-1}$ and $-1.23 \times 10^{-3} \text{ kbar}^{-1}$ at $T < 10$ K for (TSeT)₂Cl²⁶ and (TMTSF)₂ClO₄,²⁷ respectively, in the direction perpendicular to the (TSeT)₂Cl or (TMTSF)₂ClO₄ chains. Using these values of α and the value $(d(\ln T_C)/dP) \approx 0.019 \text{ kbar}^{-1}$ reported in this work, we obtain values for n of 11.6 and 15.4, respectively. These values of n are clearly different from $n = 3$, which corresponds to the simplest dipolar interaction model.²⁸ This fact gives grounds to expect that the dipolar interaction alone cannot explain the type of magnetic interchain interaction in compounds of this series, and that a contribution of the strong enough nearest-neighbors magnetic exchange interaction^{29,30} (with $n \approx 12$) should be also involved in the consideration, as was suggested by A. Caneschi et al.¹⁵

In light of the dramatic observed increase of the T_C , and keeping in mind that this fact might result mainly from a large compressibility of these quasi-1-D materials (especially in the direction perpendicular to the chains), we have also reviewed the dependence of the T_C on the averaged interchain nearest-neighbors-coupling Mn–Mn bridge length ($\langle l \rangle$) in other coordination complexes of this family.

To evaluate the averaged interchain nearest-neighbors Mn–Mn bridge length ($\langle l \rangle$) for compounds of this series, we have taken the six or eight Mn–Mn nearest-neighbor distances from the structures for the five compounds in refs 15, 16, 20, and 21, which are all the compounds of this type reported with a primary structure described by a polymeric 2₁ chain.³¹ The distance l was defined to be the shortest Mn–Mn center-to-center distance between any nearest-neighbor chains. Assuming in general the same type of the $T_C(\langle l \rangle)$ dependence as mentioned above: $T_C \propto (1/\langle l \rangle)^n$, we plot in Figure 6 the $\ln(T_C)$ vs $\ln(1/\langle l \rangle)$ values for these selected five compounds.

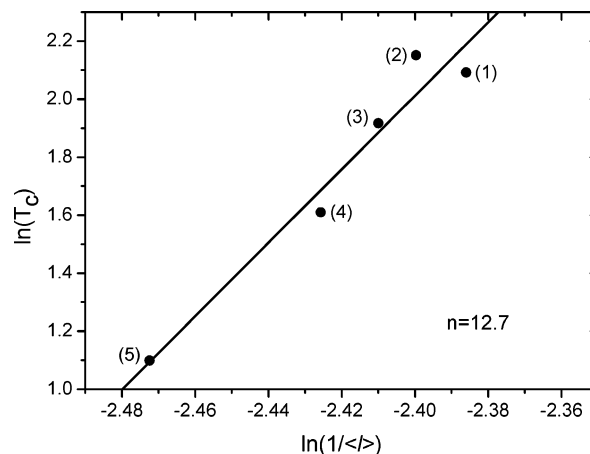


Figure 6. Variation of $\ln(T_C)$ as a function of $\ln(1/\langle l \rangle)$, where $\langle l \rangle$ is the averaged interchain nearest-neighbors Mn–Mn bridge length, for manganese(II) hexafluoroacetylacetonate coordination complexes of purely organic α -nitronyl nitroxide. The different data correspond to the following complexes: (1) [EtNN–Mn(hfac)₂]₂;²⁰ (2) [n-PrNN–Mn(hfac)₂]₂;²⁰ (3) [4-TolNN–Mn(hfac)₂]₂;²¹ (4) [4-Me₂NPhNN–Mn(hfac)₂]₂;¹⁵ (5) [(R)-3MLNN–Mn(hfac)₂]₂.¹⁶ See text for details.

Inspection of Figure 6 immediately reveals that—for all reviewed compound—a simple relationship $T_C \propto (1/\langle l \rangle)^n$ is fulfilled. From the data in Figure 6, we extract $n \approx 12.7$; this indicates that interchain coupling in this variety of compounds is given by a strong power of the interchain nearest-neighbor Mn–Mn distance. It is important to notice that this observation, in agreement with the results obtained from our experimental pressure-dependent measurements of T_C , evidently supports the suggestion that interchain magnetic coupling—which leads to 3-D ferromagnetic ordering at $T_C \propto (1/\langle l \rangle)^n$, with $n > 11$ —appears to be mainly mediated by exchange interactions. The pathway of this magnetic interaction must involve weak noncovalent interactions between atoms with very low spin density in different chains, since there are no strong specific pathways of orbital overlap and the majority of the spin density is centered at the core of the chains [on the Mn(II) ions and over the conjugated O–N–C–N–O group in the radicals].

Before closing, we would like to comment on an important issue, signaled by one of the reviewers of this manuscript, which lies beyond the scope of the presented results. Throughout the manuscript, motivated by the results and models reported in ref 16, we have assumed that the interchain coupling is ferromagnetic. In fact, the value of the saturation magnetization and the absence of a measurable high-field differential susceptibility in the magnetization curves in ref 16 strongly point in favor of a ferromagnetic ordering rather than a hypothetically canted structure in interchain antiferromagnetic coupling scenario. However, we should accept that these features are observed in (albeit small) in-field measurements, and thus, they do not exclude that in zero-field conditions other interchain ordering might be more favorable. In any event, the experimental data reported here, in particular the pressure dependence of the magnetic susceptibility data, as well as all the data taken from literature, which allowed the discovery of the significant relationship shown by Figure 6, correspond to in-field measurements where the ferromagnetic chain ordering seems to be a more appropriate description. The main inference from the data in Figure 6 is that there is a strong dependence of the interchain coupling—and thus T_C —on the interchain distance indicating in turn a superexchange-like interaction rather than a dipolar coupling. This suggestion would remain valid in the case of any eventual discovery of antiferromagnetic interchain coupling.

Conclusion

The 3-D ferromagnetic ordering temperature of the 1-D ferromagnetic chains in the new molecular magnet [(R)-3MLNN-Mn(hfac)₂] is enhanced under pressure, thus indicating that interchain ferromagnetic interactions are reinforced under these conditions. The analysis of the experimental data obtained for this compound as well as a review of the ferromagnetic ordering temperature with respect to interchain coupling distances in closely related metallo-organic molecular magnetic materials allow us to conclude that the interchain ferromagnetic interaction varies as $J \propto (1/\langle l \rangle)^n$ with $n \approx 12$. This functional dependence of the ferromagnetic coupling on the averaged interchain nearest-neighbors Mn-Mn distance strongly suggests that interchain magnetic coupling in this family of materials is not due to the dipolar interaction alone (that is usually appealed to) but in all likelihood is mediated by exchange interactions. These results are of major relevance for the understanding, design and preparation of this type of molecular magnets since they clearly show that more direct exchange pathways between chains could substantially increase the 3-D ferromagnetic transition temperature.

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