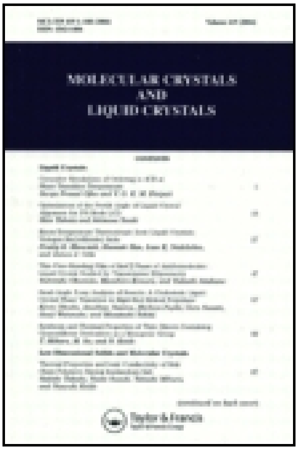

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Pressure Effect on Mn Complexes of Bisaminoxyl Radicals

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Pressure Effect on Mn Complexes of Bisaminoxyl Radicals

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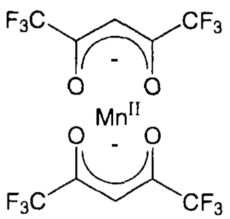
The pressure effects on magnetic properties of one-dimensional Mn complexes with 1,3-bis(*N-tert*-butylaminoxyl)benzene and 5-chloro-1,3-bis(*N-tert*-butylaminoxyl)benzene have been studied. These complexes have weak interchain interactions with different signs and the former is a metamagnet and the latter is a ferrimagnet at ambient pressure. The interchain interactions of the former is enhanced by pressurization. The transition temperature becomes higher and the critical field becomes larger with applying pressure. The closer spacing of each chains caused by pressurization, yields larger antiferromagnetic interchain interactions in this compound. On the other hand, the response to the pressure of the latter ferrimagnet, is rather complicated. The transition temperature becomes higher and the antiferromagnetic interchain interactions are induced by pressurization. The interchain exchange coupling in this compound should be sensitive to the relative orientation of the chain structure. The decrease of the ferromagnetic contribution and/or the increase of the antiferromagnetic one in the interchain interactions is brought about by pressurization.

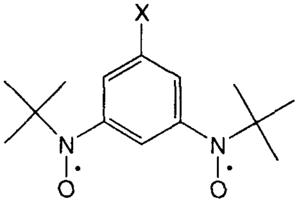
Keywords: pressure; magnetic measurements; one-dimensional magnet; metamagnet; ferrimagnet; aminoxyl radicals

INTRODUCTION

Assembling of organic polydentate ligands with transition-metals is an efficient method to construct a molecular magnet with well-defined structure[1]. The assemblage of 1,3-bis(*N*-*tert*-butylaminoxyl)benzene ($\mathbf{1}_{\mathrm{H}}$) and bis(hexafluoroacetylacetonate)manganese(II) [Mn(hfac)$_2$] yields an one-dimensional compound[2]. The 1:1 complex of [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{H}}$ is a metamagnet with $T_{\mathrm{C}} = 5.4$ K. The complexes of the halogen derivatives of 5-chloro- and 5-bromo-1,3-bis(*N*-*tert*-butylaminoxyl)benzene ($\mathbf{1}_{\mathrm{Cl}}$ and $\mathbf{1}_{\mathrm{Br}}$, respectively) with [Mn(hfac)$_2$] have similar one-dimensional chains, but undergo ferrimagnetic phase transitions at 4.8 and 5.3 K, respectively[3]. The different ground states are attributable to the different sign of the interchain interactions, which is reflecting the slight difference in the relative orientation of the chain structures.



[Mn(hfac)$_2$]



$\mathbf{1}_{\mathrm{H}}$ (X=H)
$\mathbf{1}_{\mathrm{Cl}}$ (X=Cl)

In this manuscript, the pressure effects on the magnetic properties of [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{H}}$ and [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$ are presented. For the former complex, the pressurization simply results in the enhancement of the antiferromagnetic interchain interactions, which is reflected by the higher transition temperature and critical field. On the other hand, the sign of the interchain interactions in the latter complex is changeable by pressurization. The interchain interaction in this compound should be sensitive to the relative orientation of the chain structures. Application of pressure results in the enhancement of magnetic phase transition temperature and the increase of the antiferromagnetic portion in the interchain interactions.

We first describe the difference in the crystal structures between these compounds. Then, the magnetic properties are presented and the effect of the pressure is discussed.

EXPERIMENTAL

The biradicals of $\mathbf{1}_\mathrm{H}$ and $\mathbf{1}_\mathrm{Cl}$ were synthesized[4] and the complexes with $[\mathrm{Mn(hfac)_2}]$ were obtained following the method described in the literatures[2,5]. The freshly prepared samples are mounted in a small high-pressure clamp cell made of Cu-Ti alloy, and dc and ac magnetic measurements were performed using a Quantum Design SQUID magnetometer[6].

CRYSTAL STRUCTURES

The unit cell parameters are compared in Table I. The crystal structures of these compounds are compared in Fig.1 (a) and (b). In both cases, the nearest neighbour chains have the translation symmetry along the *a*-axis. There is a slight difference in the relative orientation between chains. In the case of $[\mathrm{Mn(hfac)_2}]\cdot\mathbf{1}_\mathrm{H}$, the nearest interchain contact is the one between the oxygen atom of the *N*-*tert*-butylaminoxyl and the fluorine atom of the hfac molecule: $\mathrm{F}\cdots\mathrm{O}$ 3.04 Å. This fluorine atom is also placed near to the

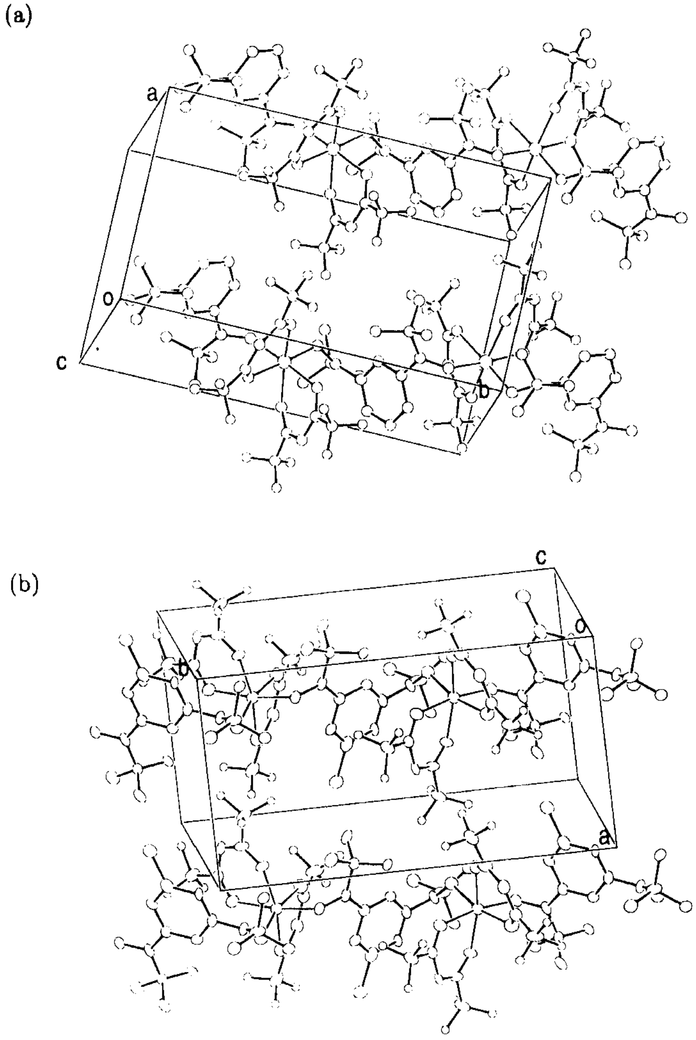


FIGURE 1 Crystal structure of (a) $[Mn(hfac)_2]\cdot\mathbf{1}_H$ and (b) $[Mn(hfac)_2]\cdot\mathbf{1}_{Cl}$.

oxygen atom of another *N-tert*-butylaminoxyl: F···O 4.19 Å. We can see the shift of the relative arrangement of each chain in [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$. One of the oxygen atom of *N-tert*-butylaminoxyl is placed near to the hfac molecule with two contacts: F···O 2.97 and 3.42 Å. These fluorine atoms are rather separated from the another *N-tert*-butylaminoxyl by the distances of F···O 4.50 and 5.24 Å. The change of the relative orientation of the chain structure is probably due to the contact between the chlorine atom and the fluorine atom of another hfac molecule: Cl···F 3.27 Å, which is close to the value of the sum of the van der Waals radii (3.15 Å).

TABLE I Unit cell parameters of [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{H}}$ and [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$. Space group is $P2_1/n$.

compound	a/Å	b/Å	c/Å	β/°	V/Å^3
[Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{H}}$[2]	9.212(3)	16.620(3)	20.088(2)	98.46(1)	3042(1)
[Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$[3]	8.953(4)	17.020(4)	20.094(5)	98.66(2)	3027(1)

MAGNETIC PROPERTIES

[Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{H}}$

The temperature dependence of the static susceptibilities at ambient pressure measured with the applied field of 5 Oe is shown in Fig. 2. The measurements after the cooling with the zero-field (ZFC)* shows abrupt increase of the susceptibilities and a sharp peak at 5.4 K.

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*The residual field is estimated by the measurements of Pb. The zero-field used is within the accuracy of ±0.1 Oe.

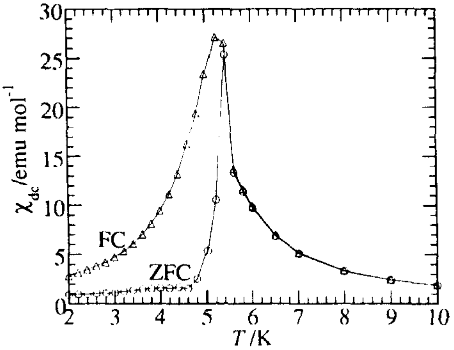

FIGURE 2 Temperature dependence of the static susceptibilities of [Mn(hfac)$_2$]·$\mathbf{1}_\mathrm{H}$ at ambient pressure suffered from ZFC (○) and FC (△).

The measurements of the ac susceptibility is also done and the sharp peaks in both the real part (χ') and the imaginary part (χ'') are observed at this temperature. We use the ac susceptibility measurements for the pressure clamp cell in order to determine the transition temperature precisely. For the reliable measurements to prevent the influence of the eddy current on the metal surface, the small frequency of *ca.* 1 Hz is used. The measurements with 1 Hz for the sample in the clamp cell without pressing give the same results for the sample mounted in a capsule. The use of the higher frequency than 40 Hz causes eddy current and the measurements in such a conditions is not reliable. Figure 3 shows the temperature dependence of the ac susceptibilities at ambient pressure and 7 kbar. Under 7 kbar, the transition temperature at which susceptibilities take a maximum, becomes higher toward 5.8 K. The magnetization isotherms at 1.8 K under ambient pressure and 7 kbar are compared in Fig. 4. The critical field also became higher toward *ca.* 600 Oe. These results means that the antiferromagnetic interchain interactions become larger by pressurization. It is suspected that pressurization brings about the shorter contacts between chains and larger exchange couplings as interchain interactions.

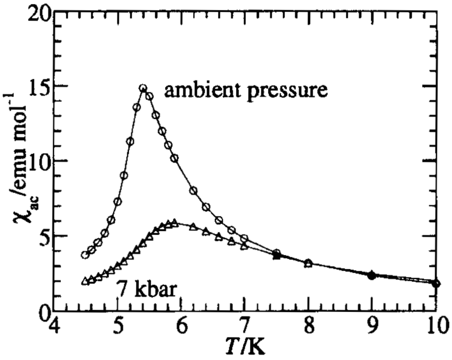

FIGURE 3 Temperature dependence of the ac susceptibilities of [Mn(hfac)$_2$]·$\mathbf{1_H}$ at ambient pressure (o) and at 7 kbar (Δ). The frequency and ac amplitude are 1 Hz and 5 Oe, respectively.

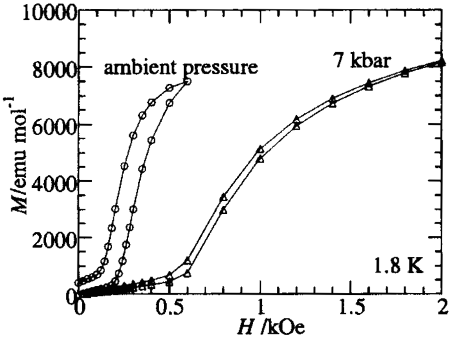

FIGURE 4 Magnetization isotherms at 1.8 K of [Mn(hfac)$_2$]·$\mathbf{1_H}$ at ambient pressure (o) and at 7 kbar (Δ).

[Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$

The temperature dependence of the ac susceptibilities at ambient pressure diverges below *ca.* 5 K, and the maximum slope of χ' is seen at 4.8 K, below which χ'' takes finite values. The magnetization isotherm at 1.8 K shows rapid saturation below 400 Oe. Therefore, [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$ at ambient pressure is characterized to a ferrimagnet with $T_C = 4.8$ K.

Figure 5 shows the temperature dependence of the ac susceptibilities of this compound under 7 kbar. The characteristic is a broad peak at 5.6 K. The magnetization isotherm at 1.8 K under 7 kbar is compared with the one at ambient pressure in Fig. 6. The saturation rate under 7 kbar below *ca.* 4 kOe is slower than the one under ambient pressure. These behaviour suggests the appearance of the antiferromagnetic distribution in the interchain interactions. However, the magnetization process under 7 kbar exhibits a hysteresis loop. As is shown in Fig. 7, the magnetization

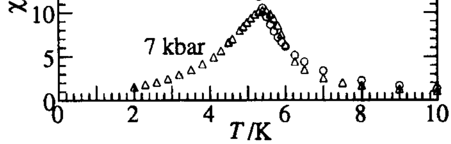

FIGURE 5 Temperature dependence of the ac susceptibilities of [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$ at ambient pressure (o) and at 7 kbar (Δ).

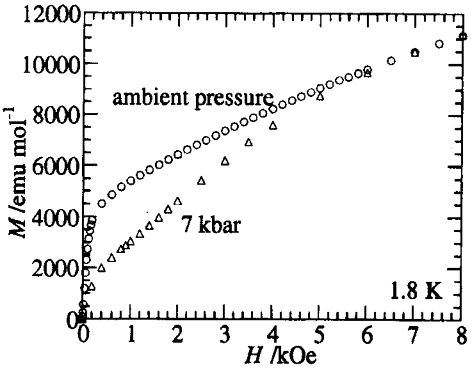

FIGURE 6 Magnetization isotherms at 1.8 K of [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$ at ambient pressure (o) and at 7 kbar (Δ).

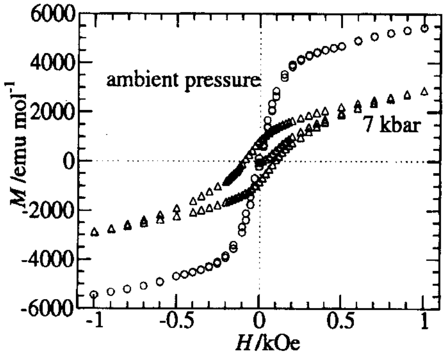

FIGURE 7 Hysteresis loops of magnetization at 1.8 K of [Mn(hfac)$_2$]·$\mathbf{1}_{\mathrm{Cl}}$ at ambient pressure (o) and at 7 kbar (Δ).

at 1.8 K under 7 kbar exhibits larger hysteresis than at ambient pressure. These observed results may be reflecting the intermediate state between the ferrimagnetic and metamagnetic ones. The competition between the ferromagnetic and antiferromagnetic interactions is suspected. For the clear observation of the metamagnetic behaviour in $[\mathrm{Mn(hfac)_2}]\mathbf{1}_{\mathrm{Cl}}$, needed is the application of larger pressure than 7 kbar.

CONCLUSIONS

The magnetic properties under pressure have been studied for one-dimensional magnets with similar crystal structures. In the present experiments, pressurization works to increase the antiferromagnetic interactions and may be to reduce the ferromagnetic interactions. This can be related to the mechanism of the exchange interactions in molecular magnetism.

Acknowledgements

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