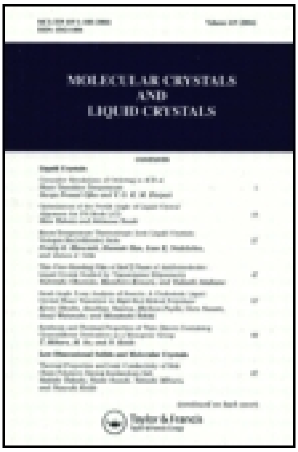

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Kentaro Suzuki, Yuko Hosokoshi & Katsuya Inoue (2003): Pressure Effects on Molecular Magnets of Mn Complexes with Bisaminoxylbenzene Derivatives, Molecular Crystals and Liquid Crystals, 379:1, 247-252

To link to this article: http://dx.doi.org/10.1080/713738650

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 247-252
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1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090552

Pressure Effects on Molecular Magnets of Mn Complexes with Bisaminoxylbenzene Derivatives

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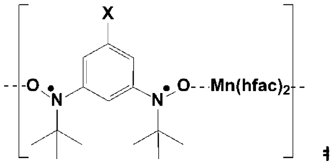
Pressure effects on the magnetic properties of a series of quasi-one-dimensional molecular magnets have been studied. The complexes of $Mn(hfac)_2$ (hfac = hexafluoroacethylacetonate) with 1,3-bis(*N*-*tert*-buthylaminoxyl)benzene and it's 5-halo- derivatives, abbreviated as $\mathbf{1}_X$ (X = H, F, Cl and Br), have almost the same ferrimagnetic chain structure. The difference is seen in the interchain molecular arrangement. The complexes of $\mathbf{1}_H$ and $\mathbf{1}_F$ are metamagnets with weak interchain antiferromagnetic interactions, whereas $\mathbf{1}_{Cl}$ and $\mathbf{1}_{Br}$ are ferrimagnets with weak interchain ferromagnetic interactions. In two metamagnets ($\mathbf{1}_H$, $\mathbf{1}_F$), the pressurization simply results in the enhancement of the interchain antiferromagnetic interactions, which is reflected by the higher transition temperature and spin-flipping field. On the other hand, in the ferrimagnet ($\mathbf{1}_{Cl}$), the metamagnetic behavior is observed under pressure. It is suggested that the subtle change of the relative arrangement of chain structures affects the interchain ferromagnetic interactions.

Keywords: Molecular magnet; quasi-one-dimensional magnet; metamagnetism; ferrimagnetism; pressure effect; aminoxyl radical

INTRODUCTION

A series of organic biradicals, 1,3-bis(*N-tert*-buthylaminoxyl) benzene and it's 5-halo- derivatives assemble with Mn(hfac)$_2$ (hfac = hexafluoroacethylacetonate) to form 1:1 complexes, $\mathbf{1}_{\mathrm{X}}$ (X = H, F, Cl and Br)[1]. These complexes involve the ferrimagnetic chain composed of S = 1 (biradical) and S = 5/2 (Mn$^{\mathrm{II}}$). The chain structure is almost identical among these complexes, but the interchain molecular arrangement is different depending on the size of the halogen atom. They are quasi-one-dimensional magnets having weak interchain interactions ($|J_{\mathrm{inter}}|/|J_{\mathrm{intra}}| \sim 10^{-3}$). The complexes of $\mathbf{1}_{\mathrm{H}}$ and $\mathbf{1}_{\mathrm{F}}$ are metamagnets with T_{N} = 5.5 and 5.2 K, respectively, due to weak interchain antiferromagnetic interactions. In the case of $\mathbf{1}_{\mathrm{Cl}}$ and $\mathbf{1}_{\mathrm{Br}}$, the interchain interactions are ferromagnetic and the ferrimagnetic phase transition is observed at T_{C} = 4.8 and 5.3 K, respectively. We have started to study the pressure effects on the series compounds, aiming to change the interchain interactions and to get insight into the magnetic exchange interactions. Continuous change of the lattice under pressure is expected. Perturbation on the molecular packing will provide us the information about the mechanism and path of magnetic exchange interactions. Crossover between metamagnetic and ferrimagnetic states is interesting. In the preceding paper[2], we briefly reported the enhancement of T_{N} in $\mathbf{1}_{\mathrm{H}}$ under pressure. Complicated results of $\mathbf{1}_{\mathrm{Cl}}$ at 7 kbar was also noted. In the present paper, we describe the pressure effect on another metamagnet, $\mathbf{1}_{\mathrm{F}}$, and the magnetic behavior of $\mathbf{1}_{\mathrm{Cl}}$ in the pressure region of 2 ~ 4 kbar in detail.



$\mathbf{1}_{\mathrm{X}}$; X= H, F, Cl and Br

EXPERIMENT

The complexes of $\mathbf{1}_{\mathrm{X}}$ were prepared following the method described in the literature[1]. The freshly prepared samples (10 ~ 40 mg) were mounted with fomblin oil as pressure transmitting medium in a small high-pressure clamp cell made of Cu-Ti alloy[3], and dc and ac magnetic measurements were performed using Quantum Design SQUID magnetometers, MPMS-2 and 5S. For the ac magnetic susceptibility (χ_{ac}) measurements, the ac field of 1 Hz and 5 Oe were used. The pressure is calibrated by the superconducting transition temperature of Pb in the separate measurement, and the reproducibility is good.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of χ_{ac} of $\mathbf{1}_H$ and $\mathbf{1}_F$ at ambient and under pressure. At ambient pressure, both the real (χ') and imaginary (χ'') components show peaks at T_N =5.4 ($\mathbf{1}_H$) and 5.2 K ($\mathbf{1}_F$). At these temperatures, metamagnetic phase transitions occur. The spin-flipping fields (H_{sf}'s) are estimated to *ca.* 200 ($\mathbf{1}_H$) and *ca.* 250 Oe ($\mathbf{1}_F$) from the magnetization isotherm at 1.8 K. With increasing pressure, monotonous enhancement of T_N and H_{sf} is observed in each complex: T_N = 5.8 K and H_{sf} ~ 600 Oe for $\mathbf{1}_H$ at 7 kbar; T_N = 5.7 K and H_{sf} ~ 700 Oe for $\mathbf{1}_F$ at 6 kbar, respectively. The results mean the enhancement of interchain antiferromagnetic interactions by applied pressure. It is considered that the shrink of the lattice under pressure results in the shorter contacts and larger interchain interactions between chains. The enhancement of the antiferromagnetic interactions, proved by the higher T_N, with increasing pressure was reported in other molecular antiferromagnets[4].

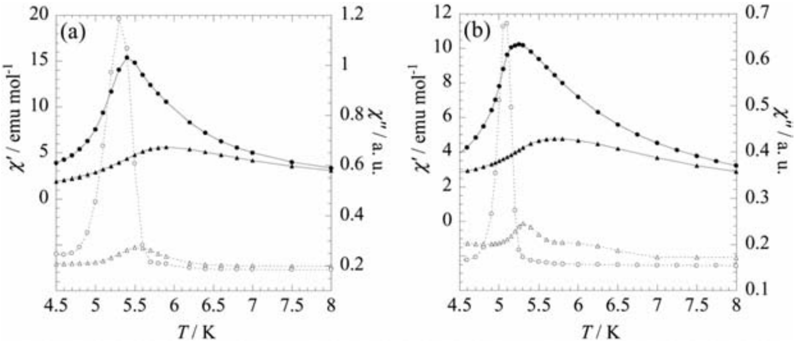


FIGURE 1 Temperature dependences of χ_{ac} at ambient pressure (χ' (●) and χ'' (○)) and under pressure (χ' (▲) and χ'' (△)) of (a) $\mathbf{1}_H$ and (b) $\mathbf{1}_F$.

Next, the pressure effects on ambient - pressure - ferrimagnets are described. Figure 2 shows the temperature dependences of χ_{ac} of $\mathbf{1}_{Cl}$ under several pressures. At ambient pressure, the abrupt increase of χ' and χ'' at T_C = 4.8 K is observed. At 1.6 kbar, ferrimagnetic behavior with T_C = 4.8 K is observed. (Figure is not shown.) Magnetic behavior is changed above 2 kbar. At 2.2 kbar, the temperature dependence of χ' shows a peak at 4.2 K and a broad shoulder at around 7.2 K. Below this temperature, rapid increase of magnetization is observed in the measurements of the field dependence. The shoulder is related to the short-range-ordered state forming ferro /ferrimagnetic domains. Above 4 kbar, metamagnetic behavior is observed below the temperature at which χ' takes a maximum. The magnetization isotherms at 4 kbar are shown in Figure 3. At 1.8 K, the bend of the magnetization curve at 200 Oe is noticeable. Below 5 K, magnetization increases rapidly below 100 Oe, and the curvature is changed above 100 Oe. The bends in magnetization curves are recognized as the maxima in the plot of field derivatives of magnetizations against the field. This spin-flipping behavior is

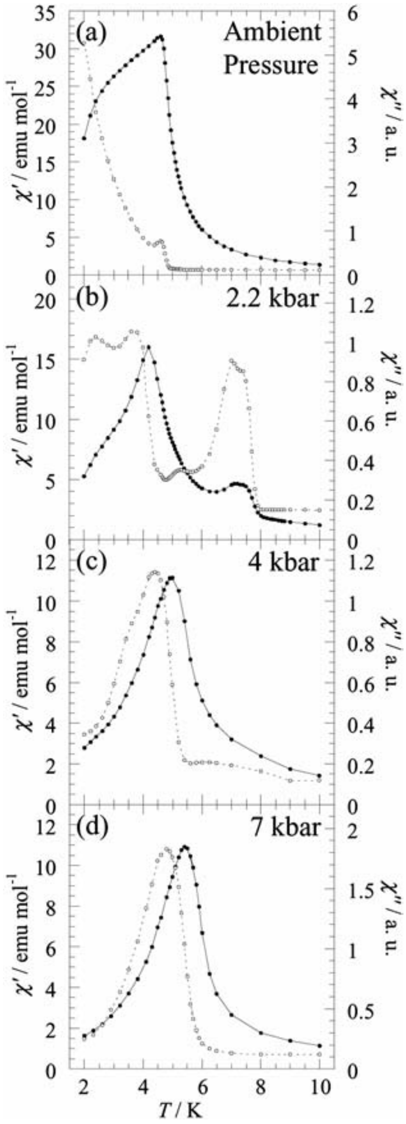


FIGURE 2 Temperature dependences of χ' (○) and χ'' (•), of $\mathbf{1}_{Cl}$ at (a) ambient pressure, (b) 2.2, (c) 4 and (d) 7 kbar.

noticeable below 5 K, at which χ' takes a maximum. New-linear increase of magnetization in the low-field region is seen below 7 K. We guess that is reflecting the short-range ferro/ferrimagnetic correlations. In the temperature dependence of χ_{ac}, we can find the increase of χ" below 8 K. At 7 kbar, there is no anomaly in the temperature dependence of χ_{ac} at around 7 K, expect for the field dependence of χ". Magnetization values are rather suppressed in the low-field region, and metamagnetic behavior is observed.

In the case of $\mathbf{1}_{Br}$, the behavior under pressure is also metamagnetic. The interchain ferromagnetic interactions are not stable under pressure. It is suggested that the subtle change of the molecular arrangement under pressure reduces the intermolecular ferromagnetic interactions. It is related to the nature of the exchange interactions. The interchain ferromagnetic interactions seem to stand on the strict condition of special molecular overlap. It is a contrast to the interchain antiferromagnetic interactions in $\mathbf{1}_H$ and $\mathbf{1}_F$. Unstability of ferromagnetic interactions under pressure is also reported for organic ferromagnets, β-*p*-NPNN[5a] and *p*-Cl-C_6H_4-CH=N- TEMPO[5b].

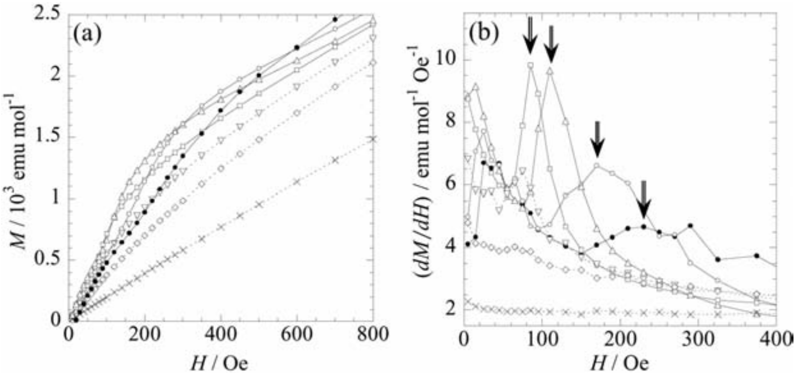


FIGURE 3 (a) Magnetization isotherms and (b) field derivatives of magnetizations against field of $\mathbf{1}_{Cl}$ at 4 kbar: 1.8 (•), 2.5 (○), 4.0(△), 5.0(□), 5.5(▽) 6.0 (◇) and 7.5 K (×).

SUMMARY

We have studied the pressure effect on the quasi-one- dimensional molecular magnets. Pressurization of the metamagnetic complexes, $\mathbf{1}_\mathrm{H}$ and $\mathbf{1}_\mathrm{F}$, yields enhancement of the interchain antiferromagnetic interactions as increasing pressure. On the other hand, ferrimagnetic complex, $\mathbf{1}_\mathrm{Cl}$, shows the metamagnetic behavior under pressure. There still remain traces of ferro/ferrimagnetic domains. It is suggested that the ferromagnetic interactions appear only for the special condition of molecular overlap, and are readily transformed into antiferromagnetic ones. Crossover between ferrimagnetic and metamagnetic states observed in $\mathbf{1}_\mathrm{Cl}$ under pressure, is probably due to the subtle change of the relative arrangement of the chain structure.

Acknowledgments
This research was supported in part by a Grand-in-Aid for scientific Research on Priority Areas (B) of Field-Induced New Quantum Phenomena in Magnetic Systems (No. 13130202) and Encouragement of Young Scientists (No. 12740389) from the Ministry of Education Culture, Sports, Science and Technology of Japan.

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