

Synthesis and magnetic properties of one-dimensional ferro- and ferrimagnetic chains made up of an alternating array of 1,3-bis(*N*-*tert*-butyl-*N*-oxyamino)benzene derivatives and Mn(II)(hfac)₂

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Received 16 March 1999; accepted 27 August 1999

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Abstract

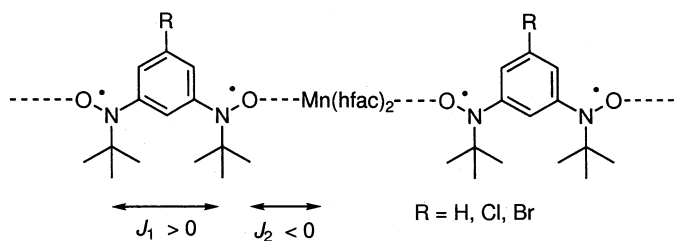
Bis(hexafluoroacetylacetonato) manganese(II), $\text{Mn}(\text{hfac})_2$, reacts with the bisnitroxide radicals, 5-*R*-1,3-bis(*N*-*tert*-butyl-*N*-oxyamino)benzene (**1_R**) (*R* = H, Cl and Br), yielding one-dimensional (1-D) polymeric complexes of formula $[\text{Mn}(\text{hfac})_2\textbf{1}_R]_n$. X-ray analysis of the complexes has shown that they crystallize in the monoclinic space group $P2_1/n$. In this structure, the manganese(II) ions and **1_R** molecules make up one-dimensional chains with the bisnitroxide radical serving as a bidentate ligand to $\text{Mn}(\text{II})(\text{hfac})_2$. The **1_H** complex orders antiferromagnetically at 5.5 K, while the **1_{Cl}** and **1_{Br}** complexes show ferrimagnetic order at 4.8 and 5.3 K, respectively. The intrachain exchange interaction parameters for a model of $S = 3/2$ ferromagnetic chains were found to be, $2J_{\text{eff}}/k = 23 \pm 2$ K in all the compounds. J_{eff} is the effective magnetic exchange interaction between units of NO-Mn-NO . A change in the sign of the interchain exchange interaction is referred to as the change of the shortest exchange path, from the $\text{Mn-F-N}(\text{tert-Bu})\text{O}^\bullet$ (**1_{Cl}** and **1_{Br}**) to $\text{N}(\text{tert-Bu})\text{O}^\bullet\text{-F-N}(\text{tert-Bu})\text{O}^\bullet$ (**1_H**) © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Molecular based magnet; Low dimensional magnet; Manganese complex; Triplet organic radical

1. Introduction

Construction of molecular based magnetic materials that have well-defined one- or two-dimensional (1-, 2-D) magnetic structure is a scientific subject of increasing interest [1–5]. Heterospin systems consisting of paramagnetic transition metal ions and organic free radicals as ligands constitute one of the mainstreams of such studies. Several of these materials have been established to have a finite critical temperature of ferro- or ferrimagnetic transitions [6–9]. The ligands employed are often organic monoradicals that have two ligating sites, e.g. semiquinones [8] and nitronylnitroxides [6,7].

We have introduced a new strategy of employing π -conjugated polynitroxides as ligands in which the 2p-spins of the NO groups interact ferromagnetically ($J_1 > 0$) (Chart I) [9]. The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighboring spins may be readily tuned by this strategy. Therefore, we report here on fabricated 1-D compounds made up of



Scheme 1.

5-substituted-1,3-phenylenebisnitroxide $\mathbf{1}_R$ ($R = \text{H}$ [11], Cl and Br) and bis(hexafluoroacetylacetonato)-manganese(II), Mn(II)(hfac)_2 , and describe their magnetic properties. In these complexes, the intrachain exchange coupling between the Mn(II) ion and the nitroxide radical is antiferromagnetic ($J_2 < 0$) because the 3d orbital of Mn(II) and the 2p orbital of nitroxide have a considerable overlap in the coordination bond. It has been established that the free biradical $\mathbf{1}_H$ has a triplet ground state with a large intramolecular ferromagnetic coupling of $J_1/k_B \gg 300$ K [10], where J_1 is defined as an intramolecular exchange coupling parameter in the Heisenberg Hamiltonian $H = -2J'S_aS_b$ for the NO group spin operators S_a and S_b of the biradical molecule. A similarly large intramolecular exchange interaction is expected for the other biradicals of $\mathbf{1}_{Cl}$ and $\mathbf{1}_{Br}$. Depending on the nature of the additional interchain interaction, the chain polymers are expected to become an antiferromagnet or a ferri/ferromagnet. The results obtained here will be of use in establishing a design strategy for tailored three-dimensional (3-D) magnetic structures with high transition temperatures on the basis of magnetic metal ions and high-spin organic polyradicals.

2. Crystal structure

2.1. Synthesis

A sample of $\text{Mn(hfac)}_2 \cdot \text{H}_2\text{O}$ (12 mmol) was suspended in 30 ml of *n*-heptane, and the mixture was refluxed to remove water by azeotropic distillation. To the cooled solution were added 12 mmol of the $\mathbf{1}_R$ radical in 10 ml of dichloromethane. The mixed solution was concentrated under reduced pressure to ca. 5 ml to give black needles from a deep-brown solution. A large single crystal grew from the $\mathbf{1}_H$ complex, while the other $\mathbf{1}_{Cl}$ and $\mathbf{1}_{Br}$ complexes were obtained in thin needles.

2.2. X-ray crystal structure analysis

Crystals were obtained as described below, selected and mounted on glass fibers using epoxy cement. The crystals were optically centered on a Rigaku AFC series diffractometer for the complexes of $\mathbf{1}_H$ and $\mathbf{1}_{Br}$ and a R-axis-IV imaging plate system for the complex of $\mathbf{1}_{Cl}$. X-ray data were collected using graphite-monochromated Mo-K α radiation. The unit cells were determined by a least-squares analysis of the setting angles of 25 carefully centered reflections in the range $35.22 < 2\theta < 40.02^\circ$ for the complex of $\mathbf{1}_H$ and $16.42 < 2\theta < 19.38^\circ$ for the complex of $\mathbf{1}_{Br}$. The R-axis-IV data processing software was used for data processing of $\mathbf{1}_{Cl}$ complex. Data were collected as indicated in Table 1, and the structures were solved and refined using the crystallographic program package TEXSAN version 2.0 from the Molecular Structure Corporation. The structure of all three compounds was solved in the monoclinic $P2_1/n$ space group (No. 14) with $Z = 4$. All non-hydrogen atoms were refined anisotropically. The crystal structure data are listed in Table 1.

Table 1

Crystallographic data for the $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_R$ complexes ($R = \text{H, Br and Cl}$)

	$\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_H$	$\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{Cl}$	$\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{Br}$
Empirical formula	$\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_6\text{F}_{12}\text{Mn}$	$\text{C}_{24}\text{H}_{23}\text{Cl}_1\text{N}_2\text{O}_6\text{F}_{12}\text{Mn}$	$\text{C}_{24}\text{H}_{23}\text{Br}_1\text{N}_2\text{O}_6\text{F}_{12}\text{Mn}$
Formula weight	719.38	753.83	798.28
a (Å)	9.212(3)	8.953(4)	9.244(4)
b (Å)	16.620(3)	17.020(4)	17.155(5)
c (Å)	20.088(2)	20.094(5)	20.431(7)
β (°)	98.46(1)	98.66(2)	99.56(3)
V (Å ³)	3042(1)	3027(1)	3195(1)
Z	4	4	4
Crystal dimensions (mm ³)	$0.30 \times 0.15 \times 0.95$	$0.05 \times 0.10 \times 0.10$	$0.20 \times 0.20 \times 0.40$
Diffractometer	Rigaku AFC5R	Rigaku Raxis-IV	Rigaku AFC7R
D_{calc} (g cm ⁻³)	1.571	1.654	1.662
Hydrogen	Refined	Fixed calculation	Fixed calculation
Observations	3256	2844	1771
Variables	434	415	415
R	0.055	0.106	0.064
R_w	0.058	0.122	0.026
GOF	1.90	2.95	2.51

The X-ray crystal structure of the $\mathbf{1}_R$ complexes revealed that the manganese(II) ions have an octahedral coordination with four oxygen atoms of two (hfac) anions and two oxygen atoms of two nitroxide groups. The latter are bound to the Mn(II) ion in a *cis*-configuration. As a result, the Mn ions and biradical molecules form a zig-zag 1-D polymeric chain structure along the crystal axis b . A closer inspection has shown that all the hexacoordinated Mn(II) ions have either Δ or Λ configuration along a given chain. Two *tert*-butylnitroxide groups are rotated out of the phenylene ring plane in a conrotatory manner but with different angles;

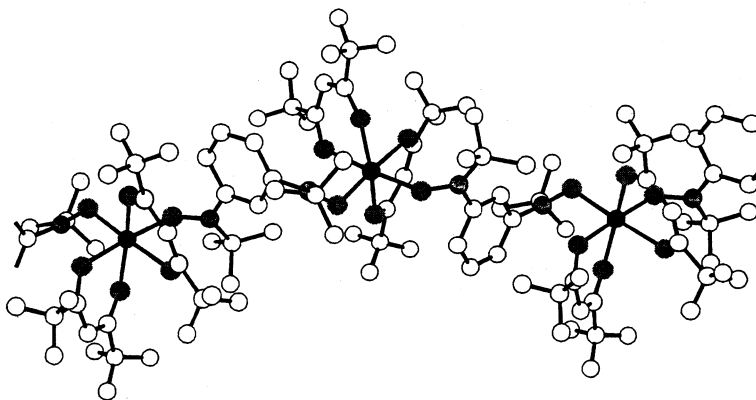


Fig. 1. A view of a 1-D chain formed by a bisnitroxide $\mathbf{1}_H$ and Mn(II)(hfac)_2 . The chain having the hexacoordinated Mn(II)s in the Δ configuration is shown.

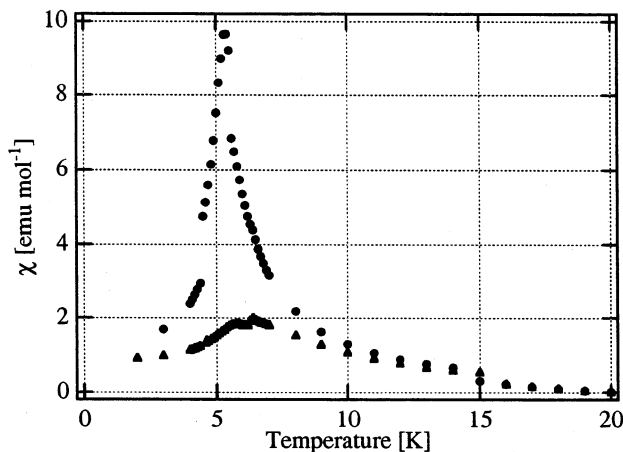


Fig. 2. The temperature dependencies of the magnetic susceptibility of a single crystal of $\text{Mn(II)(hfac)}_2 \cdot 1\text{H}$ along (○) and perpendicular (△) to the crystal c -axis measured in 5 Oe.

each 1_R molecule in the crystal has no symmetry element and is therefore chiral, i.e. R or S . The 1-D polymeric chains are therefore isotactic as all units with the same chirality reside in a given chain (Fig. 1). The crystal lattice as a whole is achiral as an enantiomeric chain is present. The Mn(II) ions on the neighboring chains are separated at least by 9.2 Å.

3. Magnetic properties

Magnetic susceptibility was measured between 1.8 and 350 K by using a Quantum Design SQUID magnetometer in fields up to 5 T.

SQUID measurements. Polycrystalline samples (ca. 30 mg) were placed in a Japanese pharmacopoeia # 5 gel capsule. The background data of the capsule were measured separately and subtracted from the sample-in-cell data. The single crystal of the 1_H complex in approximate dimensions of $1 \times 0.8 \times 6 \text{ mm}^3$ was measured by using a Quantum Design sample rotator M101C.

3.1. Ordered state

The complex $\text{Mn(II)(hfac)}_2 \cdot 1_H$ has an antiferromagnetic ground state. The temperature dependence of the low-field susceptibility shows a sharp cusp at $T_N = 5.5 \text{ K}$ (Fig. 2). From these data it follows that the c -projection of the magnetization vector, M_c (M with index ' c '), is larger than M_a (M with index ' a '). As in many other molecular complexes with bivalent manganese, the anisotropy of paramagnetic susceptibility can also be detected in $\text{Mn(II)(hfac)}_2 \cdot 1_H$.

The magnetization reaches the saturation value of ca. $3 \mu_B$ at 30 000 Oe, which agrees well with the theoretical limit $S_{\text{tot}} = 5/2 - 2/2$ for a strong antiferromagnetic

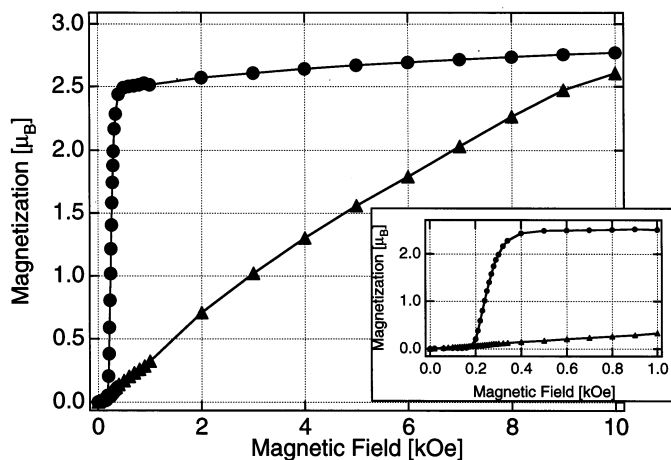


Fig. 3. Field dependence of the magnetization of a single crystal of $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1_H}$ along (○) (easy axis) and perpendicular (△) (hard axis) to the crystal c -axis. Inset shows magnetic field range of 0–1 kOe.

exchange coupling between the manganese(II) ion and ligand $\mathbf{1_H}$ ($J_2 < 0$ in Chart I). The field dependence of magnetization shows typical metamagnetic behavior (Fig. 3). Thus both, the interchain and basic intrachain, exchange interactions are negative in the $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1_H}$ complex.

The low-field susceptibilities of the $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1_{Cl}}$ and $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1_{Br}}$ complexes with the ferrimagnetic ground state as a function of temperature are shown in Fig. 4.

The values of T_C were determined as 4.8 and 5.3 K for $\mathbf{1_{Cl}}$ and $\mathbf{1_{Br}}$, respectively. Below T_C the magnetic behavior of both compounds is very similar. The magnetization at 1.8 K shows saturation at about 30 000 Oe with a maximal value of ca. $3 \mu_B$ (Fig. 5), which corresponds to the antiparallel alignment of the Mn and NO group

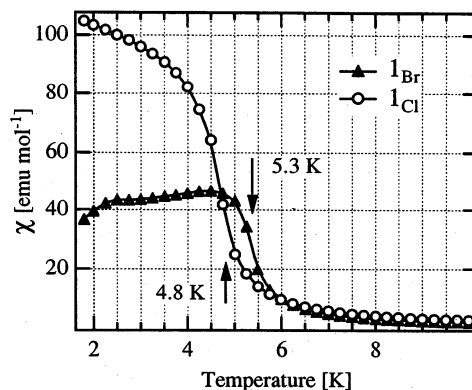


Fig. 4. Temperature dependence of the low-field susceptibility (5 Oe) for the ferrimagnetic complexes $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1_{Cl}}$ and $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1_{Br}}$.

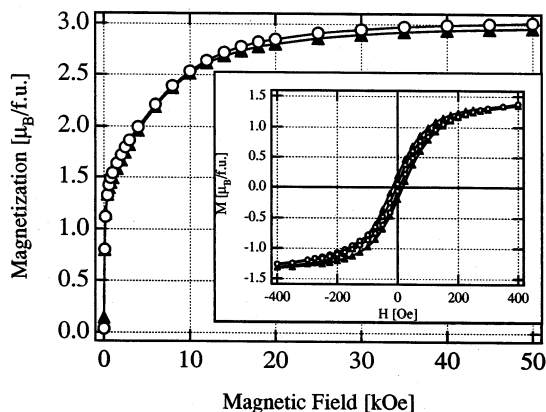


Fig. 5. Magnetization curves of $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{Cl}}$ (○) and $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{Br}}$ (Δ) at 1.7 K. Inset shows the low-field cycling.

spins. The compounds show narrow hysteresis with a coercive force of less than 20 Oe (inset of Fig. 5).

3.2. Paramagnetic range

The product of the molar susceptibility and temperature, $\chi_m T$, for all the $\mathbf{1}_{\text{R}}$ complexes increases steadily with decreasing temperature and passes over a maximum at 8–9 K. These dependencies coincide in the paramagnetic range, therefore in Fig. 6 only the data for $\{\text{Mn(hfac)}_2\} \cdot \mathbf{1}_{\text{H}}$ are displayed.

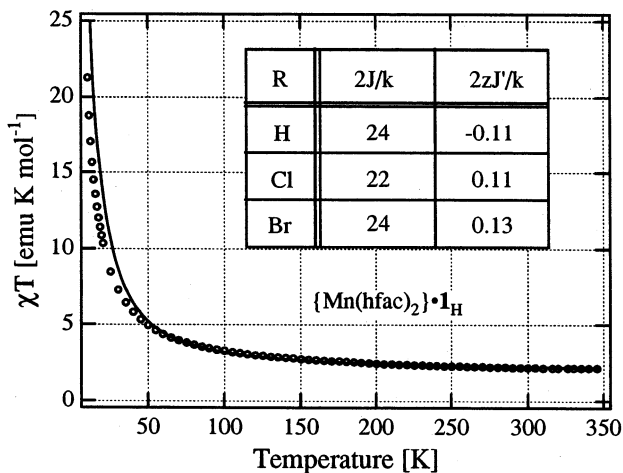


Fig. 6. Temperature dependence of the product $\chi_m T$ for the $\{\text{Mn(hfac)}_2\} \cdot \mathbf{1}_{\text{H}}$ complex (circle symbols). The solid line is a fit by the use of Eq. (2). In the inset table the fit parameters are listed for this compound and for those of $\mathbf{1}_{\text{Cl}}$ and $\mathbf{1}_{\text{Br}}$ complexes.

The $\{\text{Mn}(\text{hfac})_2\} \cdot \mathbf{1}_R$ compounds under consideration have three-spin periodicity along the 1-D chains and the extensive analysis of intrachain exchange interactions requires numerical calculations using the spin Hamiltonian $H = -2J_1 \sum_i (s_{3i-2}s_{3i-1} + s_{3i-2}s_{3i} + \alpha s_{3i}s_{3i+1})$ with $\alpha = J_2/J_1$, s and S being the NO group and Mn^{2+} spin operators, respectively. However, considering the high temperature value of $\chi_m T$ and low-temperature saturation magnetization some preliminary conclusions can be made about the strength of intrachain spin–spin coupling. As a matter of fact, taking into account the saturation magnetization value in the ordered state, two configurations should be considered: (i) ferrimagnetic chains formed by the 2/2 total spins of biradicals antiferromagnetically coupled with the 5/2 spins of Mn^{2+} ions; and (ii) ferromagnetic chains formed by the spin species consisting of two NO groups of different biradicals bridged by Mn^{2+} ions, i.e. $S = 3/2$ ferromagnetic chains. The former configuration should yield a characteristic high temperature minimum in χT versus T with the value approaching $5.38 \text{ emu K mol}^{-1}$, while for the latter one the high temperature value of $1.875 \text{ emu K mol}^{-1}$ is expected. The observed $\chi_m T$ values at 300 K vary between 2.2 and $2.4 \text{ emu K mol}^{-1}$, which is slightly larger than the theoretical limit of $1.88 \text{ emu K mol}^{-1}$ expected for $S = 3/2$ ferromagnetic chain compounds. Hence, the basic intrachain exchange interaction in $\{\text{Mn}(\text{hfac})_2\} \cdot \mathbf{1}_R$ compounds can be determined assuming a ferromagnetic chain structure with $S = 3/2$.

For the analysis the classical-spin approximation was used and the experimental χT dependencies were treated by the expression [16]

$$\chi_m T = N \frac{g^2 \mu_B^2}{3k} S(S+1) \frac{1 + U(T/T_0)}{1 - U(T/T_0)} \quad (2)$$

where $U(T/T_0) = \coth(T_0/T) - T/T_0$, $T_0 = (2J/k)S(S+1)$ and all the other symbols have their usual meaning. A comparative analysis of the behavior of classical and quantum ferro- or ferrimagnetic chains [12] showed that both approaches yield similar values for the exchange interaction parameter at elevated temperatures $T > 2J/k_B$. Therefore, Eq. (2) was first fitted to the experimental χT curve in the high-temperature region, then the fits were extended down to ca. 50 K. The value of $2J/k_B$ was found to be the same for all the three $\{\text{Mn}(\text{hfac})_2\} \cdot \mathbf{1}_R$ compounds with $R = \text{H}$, Cl and Br and equal to $23 \pm 2 \text{ K}$.

Using this value, the interchain exchange parameter of ferrimagnetic compounds $\text{Mn}(\text{II})(\text{hfac})_2 \cdot \mathbf{1}_{\text{Cl}}$ and $\text{Mn}(\text{II})(\text{hfac})_2 \cdot \mathbf{1}_{\text{Br}}$ was then evaluated. Near T_C , $T_0/T > 10$. Thus, taking $U(T/T_0) = 1 - T/T_0$, and introducing the interchain exchange interaction by $\chi_{\text{tot}} = 1/(\chi_m^{-1} - \lambda')$ one obtains

$$T_1 = \frac{3T_C^2}{2T_0 - T_C} \quad (3)$$

where $T_1 = (2zJ'/k)S(S+1)$. This equation reduces to that given by Richards [13] when neglecting T_C in the denominator. The evaluated values of $2J'/k$ are $+0.018 \text{ K}$ and $+0.022 \text{ K}$ for $\text{Mn}(\text{II})(\text{hfac})_2 \cdot \mathbf{1}_{\text{Cl}}$ and $\text{Mn}(\text{II})(\text{hfac})_2 \cdot \mathbf{1}_{\text{Br}}$, respectively. Thus, the ratio J'/J is $\sim 10^{-3}$ for all the complexes studied.

The Mn complexes with $\mathbf{1}_{\text{Cl}}$ and $\mathbf{1}_{\text{Br}}$ have topologically the same crystal structure as the complex of $\mathbf{1}_{\text{H}}$. From the observed intermolecular distance, the strongest interchain interaction in $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{Cl}}$ and $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{Br}}$ is judged to arise from the $\text{Mn-F-N(tert-Bu)O}^\bullet$ interaction. The Mn–F and F– $\bullet\text{ON(tert-Bu)}$ distances are 4.69(1) and 3.12 (1) Å, respectively. This type of interaction is suggested to be ferromagnetic as dictated by McConnell's theory [14,15] and the superexchange mechanism through the fluorine atom. In contrast, in $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{H}}$ the strongest interchain interaction is judged to arise from the $\text{N(tert-Bu)O}^\bullet\text{–F–N(tert-Bu)O}^\bullet$ interaction. This type of interaction is suggested to be antiferromagnetic. This argument can be confirmed by the fact that $2J'/k$ does not exhibit a regular change throughout the $\{\text{Mn(hfac)}_2\} \cdot \mathbf{1}_{\text{R}}$ series, but changes abruptly in sign when the nearest interacting pair is changed.

Note, the approach based on the replacement of a group of several spins in the multiperiodical chains by one spin species where the total S -value corresponding to the ground state must be applied with care [16]. For example, the $\{\text{Mn(hfac)}_2\}_3(\mathbf{3R})_2$ complex with triradical ($\mathbf{3R}$), which forms a space network of linked ($\mathbf{3R}$)–Mn–($\mathbf{3R}$) chains, was also successfully approximated assuming NO–Mn–NO groups to form stable spin species with $S = 3/2$ [17]. Nevertheless, in the 1-D equimolar $\{\text{Mn(hfac)}_2\}(\mathbf{3R})$ complex the interaction between the NO groups and Mn^{2+} is substantially weaker, $2J'/k$ ca. 100 K, and the effect of the excited state population far below the room temperature becomes important.

3.3. ESR measurements

The ESR spectra were recorded on a Bruker ESP 300 X-band (9.4 GHz) spectrometer equipped with a Hewlett–Packard 5350B microwave frequency counter. An Oxford OX2-0DX liquid helium cryostat system was fitted for the low-temperature measurements.

The polycrystalline samples of $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{R}}$ showed broad singlet EPR spectra at room temperature with $\Delta H_{\text{pp}} = 303$ G, $g = 2.0055$ for $\text{R} = \text{H}$, $\Delta H_{\text{pp}} = 315$ G, $g = 2.0095$ for $\text{R} = \text{Cl}$ and $\Delta H_{\text{pp}} = 158$ G, $g = 2.018$ for $\text{R} = \text{Br}$. The temperature dependencies of ΔH_{pp} are shown in Fig. 7. The large ΔH_{pp} values indicate that the low-dimensional exchange interaction dominates in these crystals [18–20].

4. Conclusion

The 1-D compounds $\text{Mn(II)(hfac)}_2 \cdot \mathbf{1}_{\text{R}}$ made up of nitroxide biradicals $\mathbf{1}_{\text{R}}$ with $\text{R} = \text{H}$, Cl or Br and manganese(II) ions can be analyzed by using the conventional expression derived for ferromagnetic chains assuming the NO groups of different radicals from stable spin species with Mn^{2+} ($S = 3/2$). The value of the intrachain exchange parameter $2J/k_B = 23$ K does not depend on the type of biradical. In contrast, the interchain exchange parameter can be made either positive or negative by changing the type of the nearest neighbor interaction pathway, Mn–F–N(*tert*-

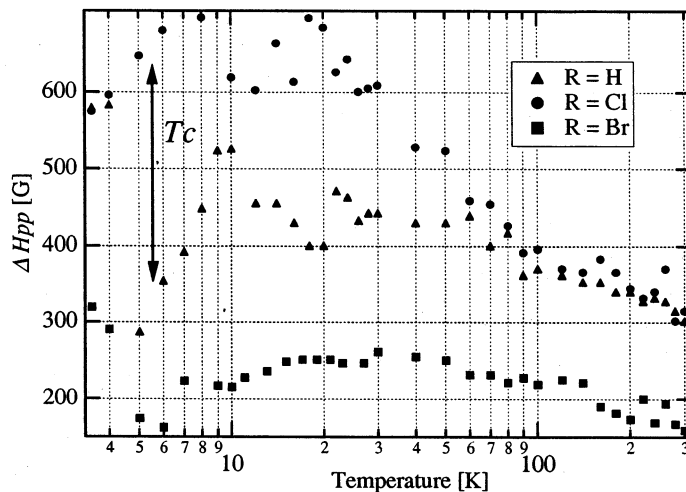


Fig. 7. Temperature dependence of ΔH_{pp} for the $\{\text{Mn}(\text{hfac})_2\} \cdot \mathbf{1}_R$ complexes ($R = \text{H}$, Cl and Br).

$\text{Bu})\text{O}^\bullet$ or $\text{N}(\text{tert-Bu})\text{O}^\bullet\text{--F--N}(\text{tert-Bu})\text{O}^\bullet$, respectively. Therefore in the complexes with $\mathbf{1}_{\text{Cl}}$ and $\mathbf{1}_{\text{Br}}$ a ferri/ferromagnetic ground state is stabilized, while the complex with $\mathbf{1}_{\text{H}}$ is an antiferromagnet. Due to a weak interchain exchange interaction the antiferromagnetic complex $\text{Mn}(\text{II})(\text{hfac})_2 \cdot \mathbf{1}_{\text{H}}$ shows a metamagnetic behavior characteristic for highly anisotropic magnetic materials.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 10146101) from the Ministry of Education, Science and Culture, Japan. We also thank the Japan Society for the Promotion of Science for the Special Researcher Fellowship given to A.S.M.

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