Preparation, structure, and magnetic interaction of a Mn(hfac)$_2$-bridged [2-(3-pyridyl)(nitronyl nitroxide)–Mn(hfac)$_2$]$_2$ chain complex†

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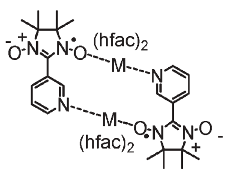
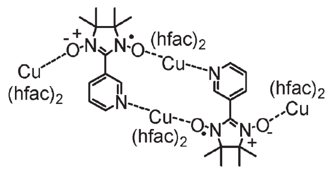
A new one-dimensional chain complex, Mn(hfac)$_2$-bridged [2-(3-pyridyl)(nitronyl nitroxide)Mn(hfac)$_2$]$_2$, was prepared and its structure and magnetic properties were elucidated; the complex exhibited a large antiferromagnetic interaction of $J_1 = -185$ K between the three Mn(II) atoms and the two nitronyl nitroxides to give $S = 13/2$ spin units and a small ferromagnetic interaction of $J_3' = +0.02$ K between these spin units at low temperatures (50–1.9 K), compatible with the theoretical analysis for model compounds.

The design and synthesis of molecule-based magnetic materials have attracted considerable attention. Magnetic metal ions and ligand-substituted nitronyl nitroxides are frequently used for this purpose and various organic–inorganic composite materials showing unique magnetic properties have been synthesized.[1] 2-(3-Pyridyl)(nitronyl nitroxide) (**1**) is one of such ligands to form various complexes with metal ions.[1–3] The typical reaction of this ligand with M(hfac)$_2$ (hfac = hexafluoroacetylacetonate) involves formation of a dimer [**1**·M(hfac)$_2$]$_2$ as illustrated in formula **A**.[1,4,5] Further bridging of the dimers with magnetic metal ions should provide an interesting one-dimensional dimer-metal chain. In this context, Rey and co-workers have prepared an interesting complex of [**1**·Cu(hfac)$_2$]$_2$·[Cu(hfac)$_2$]$_2$, whose structure involves a dimer capped by two penta-coordinated Cu(hfac)$_2$ (formula **B**).[4] Hitherto, no dimer–metal one-dimensional chain complex has been reported. We have succeeded for the first time to obtain the desired one-dimensional dimer–Mn(hfac)$_2$ chain complex, **1**$_2$·[Mn(hfac)$_2$]$_3$. We report on the preparation, structure, and the magnetic properties of **1**$_2$·[Mn(hfac)$_2$]$_3$ with the theoretical analysis of model complexes.

A solution of **1** (1 equiv.) in dichloromethane was mixed to a heptane solution of anhydrous Mn(hfac)$_2$ (1.5 equiv.).‡ After removing the solvent, the resulted blue–green powder was recrystallized from the chloroform–heptane mixture in a glove-box to give **1**$_2$·[Mn(hfac)$_2$]$_3$ in 45% yield as air-stable dark green prisms.§ The complex in a powder form showed a broad and structureless EPR signal with a width of 450 G at half height at 123 K. The structure of the complex was unequivocally determined by the crystal structure analysis.¶ The chain complex has a crystallographic repeating unit of the formula **1**·[Mn(hfac)$_2$]$_{1.5}$ and the overall structure is a one-dimensional chain along the $a + c$ direction as illustrated in Fig. 1. Each dimer in the chain is equivalently combined (in *cis* configuration) by the Mn(2) atom on the *C*2 axis. The Mn(1,2)–O bond length is within a range of 2.13–2.18 Å. The Mn(1)–N(3) bond length is 2.25 Å. The dihedral angle between the nitronyl nitroxide (NN) plane (O–N=C–N–O plane) and the pyridine ring is 38.5°. The bond angle of N(3)–Mn(1)–O(2) is 87.7°. These values are in a normal region and similar to those of the non-bridged dimer **1**$_2$·[Mn(hfac)$_2$]$_2$.[5b]



A: [**1**·M(hfac)$_2$]$_2$



B: [**1**·Cu(hfac)$_2$]$_2$ ·[Cu(hfac)$_2$]$_2$

Fig. 2 shows the temperature dependence of χ_pT, the product of molar paramagnetic susceptibility and temperature, for the chain complex, where χ_pT was calculated using the formula of **1**$_2$·[Mn(hfac)$_2$]$_3$, double the crystallographic repeating unit. The value at room temperature (15.8 emu K mol^{-1}) is already larger than 13.875 emu K mol^{-1} that corresponds to three

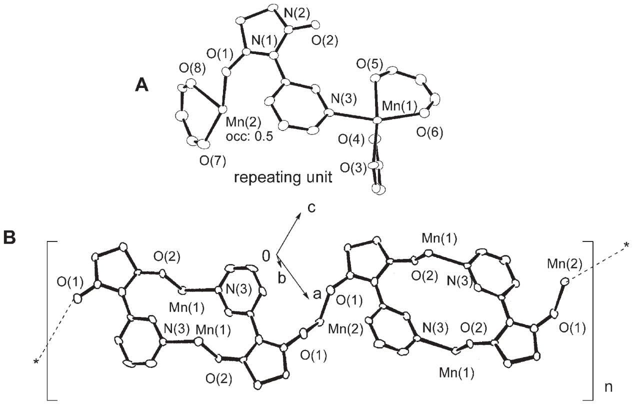


Fig. 1 Molecular structure for chain complex **1**$_2$·[Mn(hfac)$_2$]$_3$. **A**: structure of crystallographic repeating unit, **1**·[Mn(hfac)$_2$]$_{1.5}$; **B**; one-dimensional chain structure expanded by symmetry operations. Methyl groups for **A** and **B** and also hfac groups for **B** are omitted for clarity.

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† Electronic supplementary information (ESI) available: Synthesis and EPR spectrum of **1**$_2$·[Mn(hfac)$_2$]$_3$. A table of the bond lengths around the spin centers of **1**$_2$·[Mn(hfac)$_2$]$_3$ and maps of the atomic spin densities of the ground states of model I and II. See DOI: 10.1039/b618682c

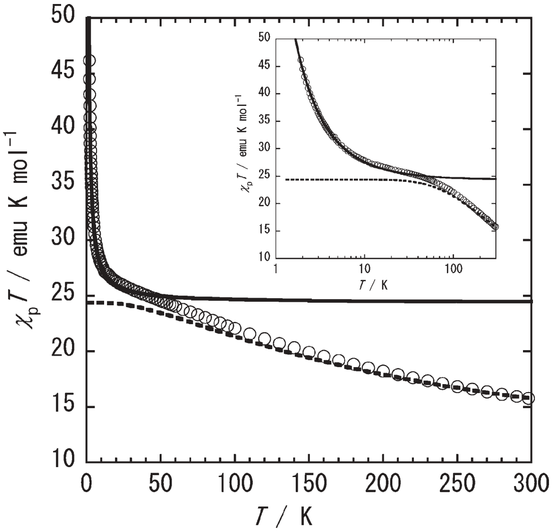
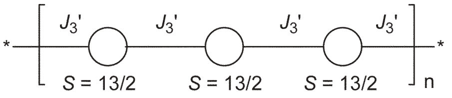


Fig. 2 $\chi_p T$ *vs.* T plots for $\mathbf{1}_2\cdot[\mathrm{Mn(hfac)_2}]_3$. The solid line shows a simulation curve according to eqn (1) with $J_3' = +0.02$ K. The dotted line shows a simulation line based on eqn (2) assuming $J_1 = J_2 = -185$ K. The inset shows $\chi_p T$ *vs.* T plots in a logarithmic scale in the *x*-axis.

$S = 5/2$ (Mn(II)) and two $S = 1/2$ (NN) spins. The $\chi_p T$ values rise moderately down to about 50 K and then much more abruptly down to 1.9 K, indicating further spin alignment between the Mn(II) and NN spins. From the previous study, it is known that the Mn(II)–NN magnetic interaction is strongly antiferromagnetic ($H = -2JS_{\mathrm{Mn}}\cdot S_{\mathrm{NN}}$, $J = -140$ to -150 K).[5b] Therefore, the gradual increase of the $\chi_p T$ values ($15.8 \rightarrow$ *ca.* 25 emu K mol^{-1}) by lowering temperature (RT → 50 K) can be ascribed to the relatively strong magnetic interaction, giving a ferrimagnetic spin alignment between three $S = 5/2$ spins (Mn(II)) and two $S = 1/2$ spins (NN) in the stoichiometry of $\mathbf{1}_2[\mathrm{Mn(hfac)_2}]_3$, as schematically shown by the rectangle in Scheme 1. The $\chi_p T$ value at 50 K is close to the predicted value for the ferrimagnetic spin alignment with the total spin of $S = 13/2$ ($\chi_p T = 24.375$ emu K mol^{-1} assuming $g = 2.00$).

Interestingly, the $\chi_p T$ value increases (*ca.* $25 \rightarrow 47$ emu K mol^{-1}) by further lowering temperatures ($50 \rightarrow 1.9$ K). This indicates spin alignment between $S = 13/2$ units in the chain. The observed ferromagnetic behavior between the $S = 13/2$ units is attributed to the local exchange interactions, J_3, between an $S = 5/2$ spin on the Mn(II) atom and an $S = 1/2$ spin of the radical **1** (Scheme 1). The interaction J_3 would be much smaller than that of the antiferromagnetic interaction between Mn(II)–NN ($J_1 = J_2 = -185$ K, *vide infra*). The effect of the weak interaction, *i.e.*, the parallel alignment of $S = 13/2$ spins, should become apparent only at low temperature. For this reason, it is reasonable to assume that the $\chi_p T$ values at low temperatures (<50 K) can be analysed using the model of equally spaced $S = 13/2$ spins coupled by ferromagnetic interaction (eqn (1)).[6] The simulation with $J_3' = +0.02$ K well reproduced the observed $\chi_p T$ values in the low temperature region (solid line in Fig. 2).



(1)

$$H = -2J_3'\sum_i \mathbf{S}^i(S = 13/2)\cdot\mathbf{S}^{i+1}(S = 13/2)$$

On the other hand, the $\chi_p T$ values in high temperatures (>*ca.* 150 K) were reproduced by a five-spin cluster model with three $S_{\mathrm{Mn}} = 5/2$ spins and two $S_{\mathrm{NN}} = 1/2$ spins in the repeating unit, as shown by the rectangle in Scheme 1, using the spin Hamiltonian:

$$H = -2J_1\mathbf{S}_{\mathrm{Mn1}}\cdot\mathbf{S}_{\mathrm{NN1}} - 2J_2\mathbf{S}_{\mathrm{NN1}}\cdot\mathbf{S}_{\mathrm{Mn2}} - 2J_2\mathbf{S}_{\mathrm{Mn2}}\cdot\mathbf{S}_{\mathrm{NN2}} - 2J_1\mathbf{S}_{\mathrm{NN2}}\cdot\mathbf{S}_{\mathrm{Mn3}} \quad (2)$$

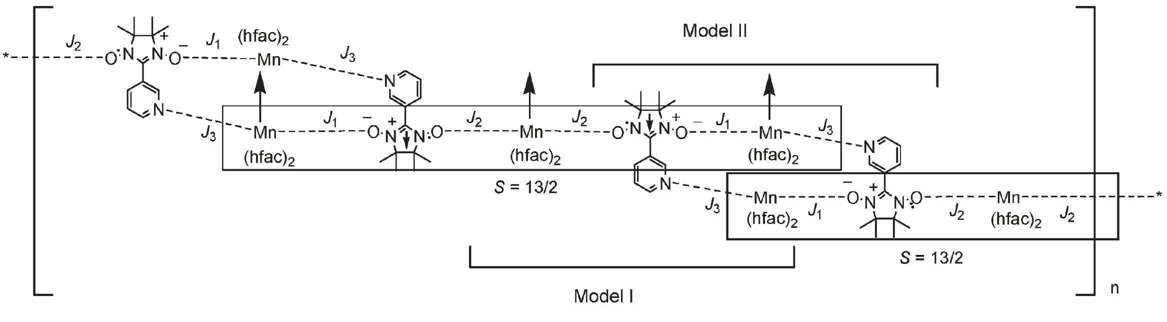
The matrix of the spin Hamiltonian (eqn (2)) was numerically diagonalized to give energy eigenvalues, from which the temperature dependence of $\chi_p T$ was calculated. The simulation assuming $J_1 = J_2 = -185$ K (dotted line in Fig. 2) well fits the observed values.‖ The $J_{1(2)}$ value is similar to the antiferromagnetic interaction of the closely related non-bridged complexes,[5b] although the absolute value of the former is slightly larger than that of the latter (-140 to -150 K). The $\chi_p T$ value (47 emu K mol^{-1}) at 1.9 K corresponds to the spin alignment a little over two magnetic repeating units.

In order to obtain theoretical insight into the magnetic interaction of J_1, J_2 and J_3 (Scheme 1), we carried out calculations using partial structures of the chain complex (model I and model II). The model structures (Scheme 2) were constructed from the X-ray geometry except for the two terminals in model I, where the nitroxide oxygen atoms are partly replaced by water molecules for simplicity.[7]**

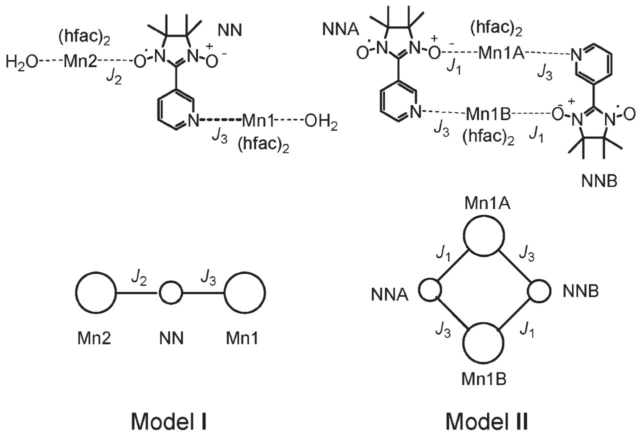
For estimation of the magnetic interaction J_{ab} values, we used Ising model spin Hamiltonian, which considers only up and down spins along the *z*-axis as follows:

$$H = -2\sum J_{ab}S_a^Z S_b^Z \quad (3)$$

where spin is localized on the sites ***a*** and ***b***.



Scheme 1



Scheme 2 Models I and II and their schematic presentation.

Table 1 Total energies and $\langle S^2\rangle$ of the considered spin states for model I and II

Model	Spin state	Total energy^a/a.u.	$\langle S^2\rangle$	J/K
I	uuu	-6992.34860418	35.7959	$J_2 = -239$ $J_3 = -1.0$
I	duu	-6992.35239052	5.7474	
I	udu	-6992.35240698	25.7482	
II	uuuu	-7620.07849434	42.0899	$J_1 = -274$ $J_3 = -1.0$
II	uddu	-7620.07852679	6.0914	
II	udud	-7620.08721584	21.9756	

^{a} Threshold of convergence was 10^{-7}/a.u. in electron density.

The exchange interactions J_2 and J_3 in model I were calculated according to eqn (4a) and (4b):

$$J_2 = \frac{E(\mathrm{duu}) - E(\mathrm{uuu})}{5} \tag{4a}$$

$$J_3 = \frac{E(\mathrm{udu}) - E(\mathrm{duu})}{5} \tag{4b}$$

where E(duu), E(uuu) *etc.* are total energies of the spin states of *down*, *up*, *up* for duu or *up*, *up*, *up* for uuu, *etc* in the sites of Mn2, NN and Mn1 in model I.

Similarly, J_1 and J_3 in Model II were calculated according to eqn (5a) and (5b):

$$J_1 = \frac{E(\mathrm{udud}) - E(\mathrm{uddu})}{10} \tag{5a}$$

$$J_3 = \frac{E(\mathrm{uddu}) - E(\mathrm{uuuu})}{10} \tag{5b}$$

where uddu, *etc* are defined as spin states showing up-down relation in the sites of Mn1A, NNB, Mn1B, NNA in model II, respectively.

The UHF-based broken symmetry calculations with ub3lyp/4–31G using Gaussian 98 program package[8] gave the results shown in Table 1.

It should be noted that negative J_3 corresponds to the positive J_3'. Furthermore, the size of calculated J_3 value cannot be directly compared to the J_3' obtained by the model of equally spaced S = 13/2 spins because of their different definitions. In spite of simplified model structures (models I and II) that may incur difficulty in quantitative estimation of the J_3 value, the calculated large negative $J_{1,2}$ and small negative J_3 are consistent with the experimental results.

Thus, we have experimentally and theoretically shown that the one-dimensional chain complex, $\mathbf{1}_2\cdot[\mathrm{Mn(hfac)_2}]_3$, reveals ferrimagnetic spin alignment in relatively high temperature region (RT → 50 K) and ferromagnetic (between S = 13/2 spins) behaviour at lower temperature (50 → 1.9 K). Study for one-dimensional dimer–metal chain complexes of the related compounds is in progress.

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‡ Azeotropic removal of coordinated water involved in commercial $\mathrm{Mn(hfac)_2}$ is essential.

§ Mp 187 °C, IR (KBr) $\nu_{\max}$/cm^{-1} 1651, 1607,1556, 1531, 1497, 1481, 1400, 1371,1329, 1256, 1207, 1146, 1097, 800, 665, 584. Anal. Found: C, 34.47; H, 1.95; N, 4.45. Calc. for $C_{54}H_{38}F_{36}Mn_3N_6O_{16}$: C, 34.58; H, 2.04; N, 4.48%. EPR (powder) g = 2.0081 as a broad and structureless signal with a width of 450 G at half height.

¶ *Crystallographic data* for $\mathbf{1}\cdot[\mathrm{Mn(hfac)_2}]_{1.5}$ ($C_{27}H_{19}F_{18}Mn_{1.5}N_3O_8$); M = 937.84, monoclinic, space group $C2/c$ (no. 15), a = 25.102(3), b = 14.1911(14), c = 22.067(3) Å, β = 113.084(5)°, V = 7231.5(15) Å^3, Z = 8, T = 93 K, unique reflections 7906, observations 3796 ($I > 2.0\sigma(I)$), R_1 =0.055, R_W = 0.069 [$I > 2\sigma(I)$]. CCDC 630084. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618682c.

‖ The two parameters J_1 and J_2 have been assumed to be the same in the simulation in order to avoid overparametrization. In the simulation, the g-factor has been fixed as g = 2.0081 as observed from the EPR spectrum.

** The geometry of the water molecules was optimized using a molecular mechanics force field. Cerius^2 (ver3.9) was used for molecular mechanics calculation using Universal Force Field parameters developed by Goddard III and co-workers.[7]

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