

# A new hetero-spin compound derived from 1,4-bis(nitronyl nitroxide)benzene and Mn(II)hexafluoroacetylacetonate for studies on molecular magnetism<sup>☆</sup>

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## Abstract

A new hetero-spin compound **1** derived from 1,4-bis(nitronyl nitroxide) benzene and Mn(II) hexafluoroacetylacetonate [Mn(hfac)<sub>2</sub>] was prepared and characterized. Its crystal structure was determined: monoclinic, *P2(1)/n*, *a* = 16.3260(7) Å, *b* = 13.7080(7) Å, *c* = 18.396(1) Å,  $\beta$  = 68.380(5)°, *V* = 3827.3(3) Å<sup>3</sup>, *Z* = 4. The intramolecular spin–spin exchange parameters for Mn(II) ion and nitronyl nitroxide unit ( $J_{12} = -108.3 \text{ cm}^{-1}$ ), two nitronyl nitroxide units ( $J_{23} = -31.0 \text{ cm}^{-1}$ ) as well as the intermolecular spin–spin coupling ( $zJ' = 4.9 \text{ cm}^{-1}$ ) were deduced based on these magnetic data measured with SQUID.

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## 1. Introduction

In recent years, studies of molecular magnetism have received more and more attention. In this field, coordination chemistry has played a very important role, exemplified by the extensive investigations of hetero-spin compounds formed between nitronyl nitroxides/nitroxides and M(hfac)<sub>2</sub> (M = Cu<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> etc., hfac = hexafluoroacetylacetonate) (see for example [1]). Magnetic chains and even bulk ferromagnetism were obtained from these studies. Experimental results reported by Inoue et al. [2] about the complexes derived from multi-nitroxides and Mn(hfac)<sub>2</sub> suggested that dimensionalities of magnetic materials could be increased if multi-nitronyl nitroxide/nitroxides with suitable topology were employed for the coordination with M(hfac)<sub>2</sub>. By now, only a few coordination compounds resulting from molecules with two nitronyl nitroxide units and

M(hfac)<sub>2</sub> have been well described. Recently, we have obtained a new four-spin coordination compound from the reaction between 1,4-bis(nitronyl nitroxide)benzene and Cu(hfac)<sub>2</sub> [3]. In this paper, we wish to report the synthesis, crystal structure and magnetic property of a new hetero-spin compound **1** derived from 1,4-bis(nitronyl nitroxide) benzene and Mn(hfac)<sub>2</sub>.

## 2. Experiment

Compound **1** was prepared similarly based on the procedure described in Ref. [3]: m.p., 153–154 °C; IR, 1257, 1203 cm<sup>-1</sup>; Anal. Calc. for C<sub>30</sub>H<sub>32</sub>MnF<sub>12</sub>N<sub>4</sub>O<sub>9</sub>: C, 41.46%; H, 3.68%; N, 6.40%; Found: C, 41.35%; H, 3.81%; N, 6.16%. The X-ray diffraction data were collected at 293 K on a Siemens P4 diffractometer with a graphite monochromator for the Mo K $\alpha$  ( $\lambda = 0.071073 \text{ \AA}$ ) radiation. Absorption correction, cell constants, and the structure solution and refinement were performed routinely. The magnetic susceptibility was measured on the bulk material (40.6 mg) in the temperature range 5–300 K with SQUID magnetometer (MPMS-7, Quantum Design). The data were corrected for the magnetization of the sample holder and the diamagnetism of the constituent atoms using Pascal constants.

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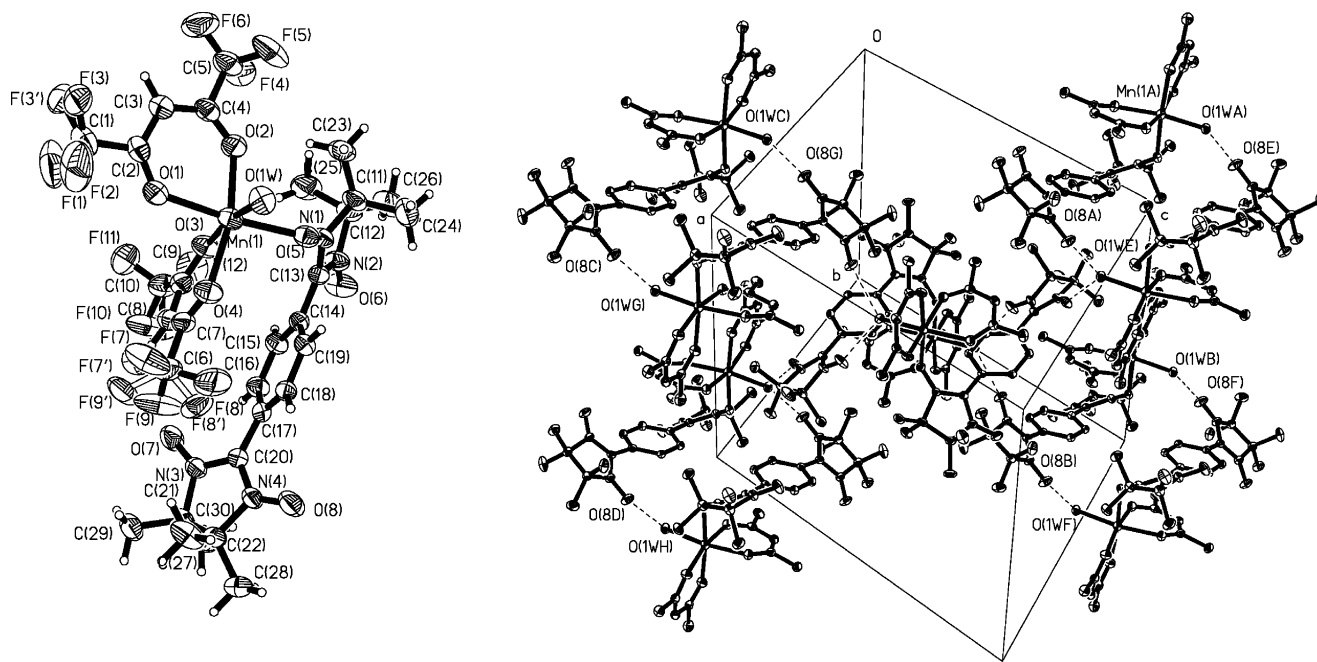


Fig. 1. Molecular structure (left) and intermolecular arrangements (right) of compound **1**.

### 3. Results and discussion

The crystal structure of compound **1** was determined by X-ray diffraction analysis.<sup>2</sup> Fig. 1 (left) shows the molecular structure of compound **1**. All the bond lengths of Mn(1)–O in compound **1** are comparable to those of the reported nitronyl nitroxide complexes with Mn(hfac)<sub>2</sub>. The Mn(1)–O(5)–N(1) angle is 126.3(4)°. For the 1,4-bis(nitronyl nitroxide) benzene unit, the bond length of N(1)–O(5) is longer than that of N(2)–O(6) due to the formation of coordination bond Mn(1)–O(5), while the bond lengths of N(3)–O(7) and N(4)–O(8) are almost identical as for most of the free nitronyl nitroxide units. Fig. 1 (right) shows the intermolecular arrangements in the crystal lattice for compound **1**. Short interatomic distances were found between the oxygen atoms of nitronyl nitroxide units and these of water molecules coordinated to the Mn(II) ions (O(8)–O(1w)', 2.71 Å). Such short interatomic contact will result in the formation of hydrogen bonds between the oxygen atoms of the free nitronyl nitroxide units and hydrogen atoms of water molecules. According to the previous results [4], such hydrogen bond may lead to intermolecular ferromagnetic coupling. This is indeed in accordance with the result of magnetic measurement for compound **1** as detailed below.

The temperature dependence of the product  $\chi T$  for compound **1** is showed in Fig. 2. At 300 K the value of  $\chi T$  is

3.82 emu mol<sup>-1</sup> K, being much smaller than the value ( $\chi T = 5.12$  emu mol<sup>-1</sup> K) expected for uncoupled spins in the case of a high-spin manganese (II) ( $g \approx 2.0$ ) and two nitronyl nitroxides. Upon lowering the temperature,  $\chi T$  falls gradually to a almost constant value of 3.57 emu mol<sup>-1</sup> K in the temperature range 100–150 K. But, below 100 K, the value of  $\chi T$  increases with further decreasing temperature reaching a maximum value of 3.70 emu mol<sup>-1</sup> K at 35 K, indicative of ferromagnetic spin–spin interactions which is probably owing to the ferromagnetic interaction between the Mn(II) ions and nitronyl nitroxides of neighboring molecules through the hydrogen bonds. On lowering the temperature further, the product  $\chi T$  decreases sharply and it reaches a value of 2.28 emu mol<sup>-1</sup> K at 5 K. This temperature dependence of the product  $\chi T$  can be well described by diagonalization of the isotropic Hamiltonian:  $H = -2J_{12}S_1S_2 - 2J_{23}S_2S_3$ , where

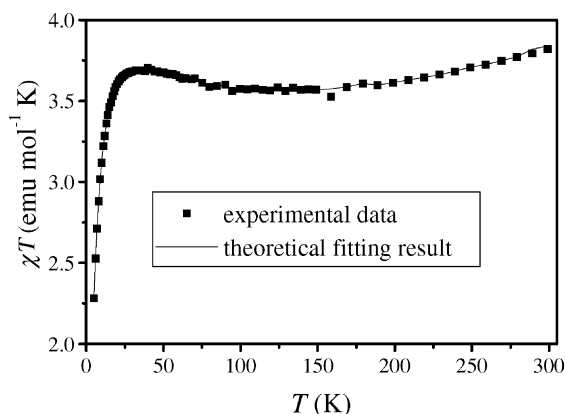


Fig. 2. Temperature dependence of product  $\chi T$  for compound **1**.

<sup>2</sup> Crystal data: C<sub>30</sub>H<sub>32</sub>F<sub>12</sub>MnN<sub>4</sub>O<sub>9</sub>,  $M = 875.54$ , monoclinic,  $P2(1)/n$ ,  $a = 16.3260(7)$  Å,  $b = 13.7080(7)$  Å,  $c = 18.396(1)$  Å,  $\beta = 68.380(5)^\circ$ ,  $V = 3827.3(3)$  Å<sup>3</sup>,  $Z = 4$ . The final cycle of full-matrix least-square refinement was based on 6603 observed reflections [ $I > 2\sigma(I)$ ] and 551 variable parameters and converged to  $R = 0.108$  and  $wR = 0.206$ .

$J_{12}$  and  $J_{23}$  represent the intramolecular exchange parameters between the Mn(II) ion and one nitronyl nitroxide unit, and two nitronyl nitroxide units, respectively. The best fit is obtained by taking into account the following parameters  $J_{12} = -108.3 \text{ cm}^{-1}$  and  $J_{23} = -31.0 \text{ cm}^{-1}$  together with a weak intermolecular ferromagnetic interaction related to  $zJ' = 4.9 \text{ cm}^{-1}$ .

#### 4. Conclusion

A new hetero-spin coordination compound **1** starting from 1,4-bis(nitronyl nitroxide)benzene and  $\text{Mn}(\text{hfac})_2$  was prepared and its crystal structure was determined. On the basis of the magnetic data measured with SQUID, the intramolecular spin–spin exchange parameters for Mn(II) ion and nitronyl nitroxide unit ( $J_{12} = -108.3 \text{ cm}^{-1}$ ), two nitronyl nitroxide units ( $J_{23} = -31.0 \text{ cm}^{-1}$ ) as well as the

intermolecular spin–spin coupling ( $zJ' = 4.9 \text{ cm}^{-1}$ ) were deduced.

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