Synthesis and magnetic properties of a new complex made up of Mn(hfac)$_2$ and a radical with a triplet ground state[†]

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A new metal-radical complex of Mn(II) made up of Mn(hfac)$_2$ and the radical 4-*N*-*tert*-butylaminoxyl-4′-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl (BIPNNNO) was synthesized. The X-ray single crystal structural analysis revealed that the complex consists of discrete molecules [Mn(hfac)$_2$]·(BIPNNNO)$_2$. The magnetic characteristics of this complex were studied and the Mn–radical and intraradical exchange integrals were evaluated: -135 ± 10 and 72 ± 5 K, respectively. These values are compared with those of complexes of Mn(hfac)$_2$ with different aminoxyl polyradicals.

The self assembled complexes made up of hexafluoroacetyacetonato manganese Mn(hfac)$_2$ and various π-conjugated aminoxyl radicals with non-zero spin states are a new class of molecular magnets with interesting magnetic properties.[1–4] We have developed a strategy of using π-conjugated high-spin oligoaminoxyl radicals that can be used as bridging ligands for paramagnetic transition metal complexes in order to assemble and align the electron spins on a macroscopic scale.[4–9] Among them one-dimensional (1D), 2D and 3D magnets were recently synthesized and characterized.[4,8,10] Two kinds of exchange interactions determine the magnetic behavior of these hetero-spin complexes, Mn(II)–NO and intraradical NO–NO interactions. It was found that at least the Mn–NO exchange varies substantially in these compounds.[8,10] Therefore, a systematic study of various new compounds of this class will enable us to review the regularities in variation of the exchange interactions.

A stable diradical, 2-[*p*-(*N*-*tert*-butylaminoxyl)phenyl]-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl (PNNNO), containing both aminoxyl radical (NO) and nitronyl nitroxide radical (NN) moieties within the same molecule, was prepared and characterized.[11] The diradical PNNNO was found to have a triplet ground state with a large intramolecular ferromagnetic coupling of $J/k_B = 319$ K, where J/k_B is defined as an intramolecular exchange parameter.[12] The magnetic interaction between the two radical moieties is controlled by chemical modification.[12] Our investigations have focused not only on the magnetic properties of these radicals but also on the use of these radicals as ligands in the synthesis of magnetic materials. In this work, we synthesized and characterized a new complex with the formula [Mn(hfac)$_2$]·(BIPNNNO)$_2$, where BIPNNNO is 4-*N*-*tert*-butylaminoxyl-4′-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl.

Experimental

The triplet diradical BIPNNNO was synthesized from dibromobiphenyl. The procedure was similar to that for PNNNO[11] and will be described elsewhere. A mixture of Mn(hfac)$_2$ and BIPNNNO was dissolved in a solvent consisting of Et$_2$O and hexane in a 1 : 2 ratio. The solution was concentrated under reduced pressure and subsequently kept at −30 °C. The reaction was completed by precipitation.

$$\mathrm{Mn(hfac)_2} + 2\,\mathrm{BIPNNNO} \xrightarrow{\mathrm{Et_2O\text{—}hexane}} [\mathrm{Mn(hfac)_2}]\cdot(\mathrm{BIPNNNO})_2 \quad (1)$$

The black crystals were filtered and dried. The complex was stable under normal conditions. The results of the elemental analysis are the following: anal. calcd for MnC$_{56}$H$_{60}$O$_{10}$F$_{12}$N$_6$: C, 53.38; H, 4.80; N, 6.67; found: C, 53.34; H, 4.69; N, 6.71.

X-Ray intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with a graphite monochromated Mo-K$_\alpha$ radiation. The structure was solved by the direct method with the program package 'teXsan' (Molecular Structure Corporation). Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.[§]

The magnetic characteristics of the complex [Mn(hfac)$_2$]·(BIPNNNO)$_2$ were studied by an MPMS 5S SQUID magnetometer in the temperature range 1.8–300 K and fields up to 5 T. The diamagnetic correction was done using Pascal's constants.

Results and discussion

The structure of a molecule of [Mn(hfac)$_2$]·(BIPNNNO)$_2$ is shown in Fig. 1. The Mn(II) ion lies on a crystallographic inversion center and is coordinated by a pair of BIPNNNO and a pair of bidentate hfac anions to afford a MnO$_6$ octahedral environment. The two BIPNNNO molecules coordinate *trans* to each other. The bond distances of Mn–O are 2.128(5) Å for the BIPNNNO radical and 2.153(5), 2.130(5) Å

[†] This article is dedicated to the memory of Professor Olivier Kahn.

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[§] Crystal data for [Mn(hfac)$_2$]·(BIPNNNO)$_2$ ($T = 293$ K): MnC$_{56}$H$_{60}$O$_{10}$F$_{12}$N$_6$, $M = 1260.06$, triclinic, space group $P\bar{1}$, $a = 11.267(3)$ Å, $b = 12.605(2)$ Å, $c = 10.661(3)$ Å, $\alpha = 99.16(1)°$, $\beta = 96.97(3)°$, $\gamma = 82.60(1)°$, $V = 1471.5(6)$ Å^3, $Z = 1$, μ(Mo-K$_\alpha$), 4348 total reflections, $R(F) = 0.078$ and $R_w(F^2) = 0.088$ for 2820 observed reflections [$I > 3.0\,\sigma(I)$] and 385 variables.

CCDC reference number 440/184. See http://www.rsc.org/suppdata/nj/b0/b001840f/ for cyrstallographic files in .cif format.

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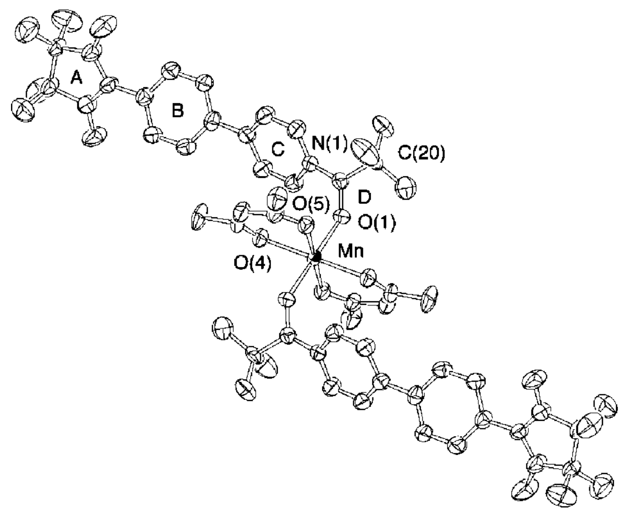

Fig. 1 ORTEP view (50% probability) of the discrete cluster of $[Mn(hfac)_2] \cdot (BIPNNNO)_2$ Hydrogen and fluorine atoms are omitted for simplicity.

for the hfac ligands. The bond angle Mn–O(1)–N(1) is 132.4(5)°. One of the characteristic structural features of $[Mn(hfac)_2] \cdot (BIPNNNO)_2$ is the coordination mode of BIPNNNO. While oxygen atoms of nitronyl nitroxide often coordinate to metal centers,[13] only the oxygen atoms of the *tert*-butyl aminoxyl moieties were found to coordinate to the Mn(II) ion. Thus, the complex does not have a polymeric structure but forms discrete clusters. Formation of a 1 : 2 complex, $[Mn(hfac)_2] \cdot (BIPNNNO)_2$, suggest that *N*-*tert*-butyl aminoxyl has a higher coordination ability to the Lewis acidic manganese ion than nitronyl nitroxide. The flexibility and structure of BIPNNNO is characterized by the dihedral angles of four approximately planar units: the nitronyl nitroxide unit (NN, A), two *para*-phenylene rings (B and C), and the C(20)–N(1)–O(1) plane of the *N*-*tert*-butylaminoxyl group (D). The dihedral angle between the former planes (A and B) is about 24.5°, and that of the two later ones (C and D) is $-29.7°$. The two phenylene rings (B and C) are twisted by 30.7° with respect to each other. In the crystal, the molecules are quasi-isolated with the shortest intermolecular N–O···O–N distance being 4.76(2) Å.

In Fig. 2, the temperature dependence of $\chi_m T$ ($\propto \mu_{eff}^2$) of the complex is shown. The low temperature value of $\chi_m T$ tends to 0.375 emu mol^{-1}, a limit for the $S = 1/2$ ground state. This value is expected for the negative Mn–NO and positive intraradical NO–NN exchange parameters. The complex remains paramagnetic down to 1.8 K. As Fig. 3 shows, the magnetization curve at this temperature can well be described by a Brillouin function for $S = 1/2$, $B_{1/2}(H/T)$ with neglect of the intercluster exchange interaction.

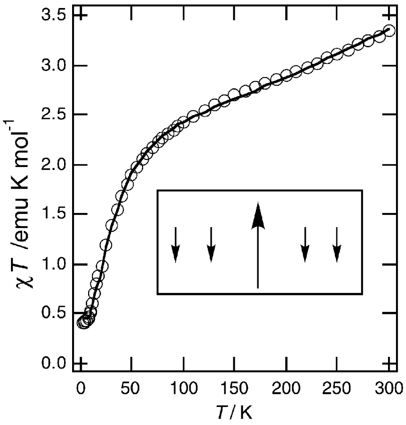

Fig. 2 Temperature dependence of $\chi_m T$ of the complex $[Mn(hfac)_2] \cdot (BIPNNNO)_2$. The experimental data are shown by symbols and the solid line is the theoretical fit (see text). The spin scheme of the complex is drawn in the frame.

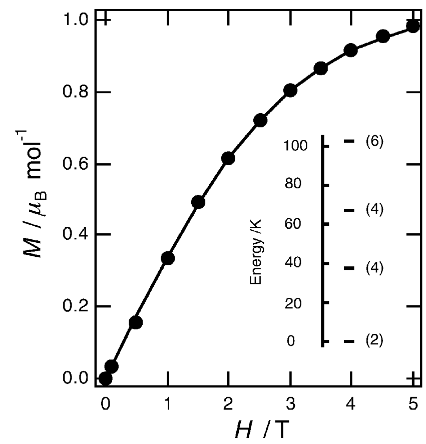

Fig. 3 Magnetization curve of $[Mn(hfac)_2] \cdot (BIPNNNO)_2$ at 1.8 K. Symbols are the experimental data and the solid line is the fit by the Brillouin function $B_{1/2}$. The inset shows the lowest energy levels of the complex. Multiplicity is given in parentheses.

The high temperature limit expected for separately acting four spins of 1/2 and one spin of 5/2, 5.875 emu mol^{-1}, is far from being reached. The character of the temperature dependence of $\chi_m T$ indicates that both the exchange interactions are comparable and new levels are successively excited with T increasing up to room temperature. The temperature variation of $\chi_m T$ was simulated numerically in the Heisenberg approximation with the use of the Van Vleck equation. The energy level scheme was found by exact diagonalization of the following Hamiltonian

$$H = -2J[S_1 \cdot S_2 + \gamma(S_2 \cdot S_3 + S_3 \cdot S_4) + S_4 \cdot S_5] \qquad (2)$$

where J and γJ are the NO–NN and Mn–NO exchange integrals, respectively, and S denotes the $S = \frac{1}{2}$ spin operator except for the S_3 which denotes the $S = 5/2$ (Mn^{2+}) spin operator. The parameter set of $J/k_B = 72 \pm 5$ K and $\gamma J/k_B = -135 \pm 10$ K well reproduces the observed data within the experimental accuracy of 10%. The low accuracy is related to the existence of a small amount of a paramagnetic impurity (less than 3%) probably due to a crystal defect and/or the contamination of $Mn(hfac)_2 \cdot 2\, H_2O$. The stationary behavior around 100 K is interpreted by the energy level scheme. The inset in Fig. 3 shows the four lowest energy levels of the complex $[Mn(hfac)_2] \cdot (BIPNNNO)_2$, which lie within the 100 K interval. They correspond to the ascending total spin-states 1/2, 3/2, 3/2, 5/2. The thermal excitations of these states provide a sharp growth of $\chi_m T$ below 100 K. The energy distance between this set and the next level is about 630 K, therefore the increase of $\chi_m T$ with temperature is weaker above 100 K.

The intraradical NO–NN exchange integral found for BIPNNNO, 72 K, is lower than that estimated for the diradical PNNNO ($J/k_B = 319$ K)[12] in which the phenyl ring B (see Fig. 1) is absent. The Mn–NO exchange parameter evaluated for this complex, -135 K, lies between the values found for other complexes with extended polymeric structures: -125 K in the 1D complex $[Mn(hfac)_2] \cdot$ **3R** $\cdot\, n$-C_6H_{14}, **3R** is a linear tris(aminoxyl)radical, bis(3-*N*-*tert*-butyl-5-*N*-*tert*-butylaminoxylphenyl)aminoxyl,[8] and -175 K in the 2D complex $[Mn(hfac)_2]_3 \cdot (\mathbf{3R_\Delta})_2 \cdot n$-$C_7H_{16}$ where $\mathbf{3R_\Delta}$ is a triangular radical, 1,3,5-tris[*p*-(*N*-*tert*-butylaminoxyl)phenyl]benzene.[10] Both compounds have *trans* coordination of the NO groups to Mn(II), similar to the complex reported in the present work. In contrast, the Mn–NO exchange parameter for the 1D complex $[Mn(hfac)_2] \cdot$ **1**, where **1** is 1,3-bis(*N*-*tert*-butylaminoxyl)benzene, in which the NO groups are coordinated in *cis* positions, is very strong, $J/k_B < -300$ K.[4] The same tendency is observed in another complex of $Mn(hfac)_2$ with *cis* coordinated NO groups, $[Mn(hfac)_2]\cdot$**2**, where **2** is a diradical, 5-*tert*-butyl-1,3-phenylenebis-(*N*-*tert*-butylaminoxylbenzene).[14] In this complex the Mn–NO interaction parameter J/k_B was found to be -270 K.

In the present case, we obtained the 1 : 2 complex with a discrete cluster structure. However, there is a possibility of obtaining complexes with different ratios depending on the complexation conditions. A linear trisaminoxyl radical, **3R**, is reported to yield 1 : 1 or 3 : 2 complexes with $Mn(hfac)_2$.[4] In the 1 : 1 complex, only two terminal *N*-*tert*-butyl aminoxyls coordinate to the Mn(II) ion, whereas in the 3 : 2 complex all the three aminoxyls coordinate to the Mn(II) ion. We are now trying other complexation conditions.

In conclusion, a complex of $Mn(hfac)_2$ with a new radical, 4-*N*-*tert*-butylaminoxyl-4′-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)biphenyl, having a triplet ground state was synthesized. A comparison with other Mn-radical complexes of this series shows that they can be classified into two groups having *trans* and *cis* coordinated NO groups with accordingly weaker and substantially stronger Mn–NO exchange interactions.

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