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Structures and Magnetic Properties of Bis(hexafluoroacetylacetonato)manganese(II) Ligated with *N*-[3- and 4-(*N*-*tert*-Butyl-*N*-oxyaminophenyl)]imidazole

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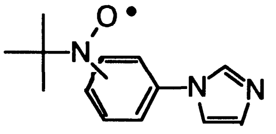
X-Ray analyses revealed that bis(hexafluoroacetylacetonato)manganese(II) forms with 1-[3- and 4-(*N*-*tert*-butyl-*N*-oxyaminophenyl)]imidazoles cyclic dimer complexes in *cis* coordination. The long-range magnetic couplings between the two spin 4/2's resulting from the strongly antiferromagnetic short-range interaction between the Mn(II) and the ligated nitroxide radical are regiospecific: antiferromagnetic for 3- and ferromagnetic for 4-nitroxide substitution on the phenyl ring.

One of the promising strategies toward the design and construction of high-T_C molecular-based magnets[1] lies in the chemical linkage of metal ions with organic free radicals.[2,3] In order for such assemblies to take the form of chains and networks, the metal ions should be coordinatively doubly unsaturated and the organic radicals should be polydentate as ligands. In the course of our study of exploring novel organic free radicals for these purposes, we have found that (1-imidazolyl)phenyl *tert*-butyl nitroxides serve as good bidentate ligands. While the expected one-dimensional chains were not obtained, they showed contrastive regiospecificity for the sign of the exchange coupling with the 3d-spin of the manganese(II) ion.

1-[3- and 4-(*N*-*tert*-Butyl-*N*-oxy-aminophenyl)]imidazoles, **3-NOIm** and **4-NOIm**, were prepared by the lithiation of the corresponding bromophenylimidazoles[4] with *n*-butyllithium followed by the reaction with 2-methyl-2-nitrosopropane. Final oxidation was made by treatment with Ag_2O. A solution of bis(hexafluoroacetylacetonato)manganese(II), Mn(hfac)$_2$, in *n*-heptane was mixed with a solution of **NOIm** in CH_2Cl_2 in a 1 : 2 molar ratio. The solvent was slowly evaporated under a stream of nitrogen gas to give dark brown crystals. Elemental analysis[5] showed that they were unexpectedly 1 : 1 complexes of Mn(hfac)$_2$ and **NOIm**, and the composition did not change even when they were mixed in a 1 : 8 molar ratio.

Crystal and molecular structures of Mn(hfac)$_2$/**3-NOIm** and Mn(hfac)$_2$/**4-NOIm** were analyzed by X-Ray diffraction.[6] Both complexes take similar cyclic dimer structures in which the oxygen of the nitroxide group and the imidazole nitrogen of one **NOIm** molecule are ligated to two different Mn(II) ions in *cis* coordination. The molecules have center of symmetry as shown by their ORTEP drawings in Fig. 1. In the molecular structure of Mn(hfac)$_2$/**4-NOIm**, the distance between the Mn(II) ions and the dihedral angles between the phenyl and imidazolyl rings and between the phenyl ring and the nitroxide group are 10.99 Å, 13°, and 27°, respectively. The corresponding distance and angles are 10.65 Å, 28°, and 24° in Mn(hfac)$_2$/**3-NOIm**. In the crystal structures of both the complexes, the shortest Mn ···· Mn separations between the nearest dimers are 8.21 and 7.54 Å for Mn(hfac)$_2$/**4-NOIm** and Mn(hfac)$_2$/**3-NOIm**, respectively.



3-: **3-NOIm**

4-: **4-NOIm**

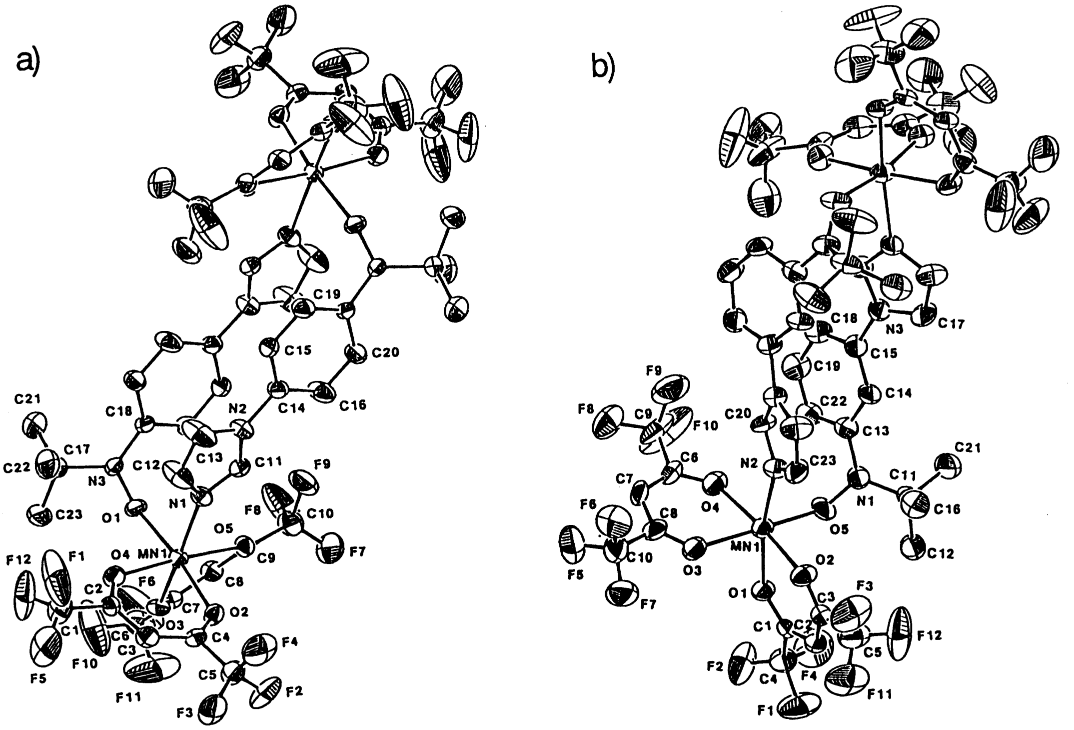


Fig. 1. ORTEP diagrams for the molecular structures of Mn(hfac)$_2$/**4-NOIm** (a) and Mn(hfac)$_2$/**3-NOIm** (b). Thermal ellipsoids are drawn at the 30% probability level.

The magnetic susceptibilities of the crystalline samples of Mn(hfac)$_2$/**3** - and **4-NOIm** were measured on a SQUID susceptometer. A constant field of 0.05 T was applied for the former in the temperature range 2 - 300 K, while fields of 0.05 and 0.01 T were used for the latter at 20 - 300 and 2- 20 K, respectively. The results are shown in Fig. 2 in the form of $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ vs. T plots for both the complexes. The effective magnetic moments $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ were 6.99 and 7.05 at 300 K for Mn(hfac)$_2$/**3-NOIm** and **4-NOIm**, respectively, and are in good agreement with $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = 6.93$ which is a theoretical spin-only value for two degenerate $S = 4/2$ (= 5/2 - 1/2) species with $g = 2$. The $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ values were nearly constant at 300 - 100 K. As the temperature was decreased below 100 K, the values for Mn(hfac)$_2$/**3-NOIm** began to decrease gradually, while those for Mn(hfac)$_2$/**4-NOIm** increased gradually and approached at 2 K a theoretical value of $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = 8.94$ for $S = 4$. The observed temperature dependences of the $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ values obviously suggest that, while the short-range magnetic coupling between the Mn(II) ion and the ligated nitroxide radical is strongly antiferromagnetic,[7,8] the long-range exchange interaction between the resultant spin 4/2's through the 1-imidazolylphenyl units are ferro- and antiferromagnetic for Mn(hfac)$_2$/**4-NOIm** and Mn(hfac)$_2$/**3-NOIm**, respectively. On the basis of such a model, we obtain eq 1 for the Boltzmann distribution of the spins among the five spin states derived from the spin Hamiltonian $H = -2JS_a{\cdot}S_b$ and $S_a = S_b = 4/2$:

$$\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = \sqrt{fg^2 \times \frac{84 + 6\exp B + 30\exp C + 180\exp D}{7 + \exp A + 3\exp B + 5\exp C + 9\exp D}} \qquad (1)$$

$$A = \frac{-12J}{k_BT} \quad B = \frac{-10J}{k_BT} \quad C = \frac{-6J}{k_BT} \quad D = \frac{8J}{k_BT}$$

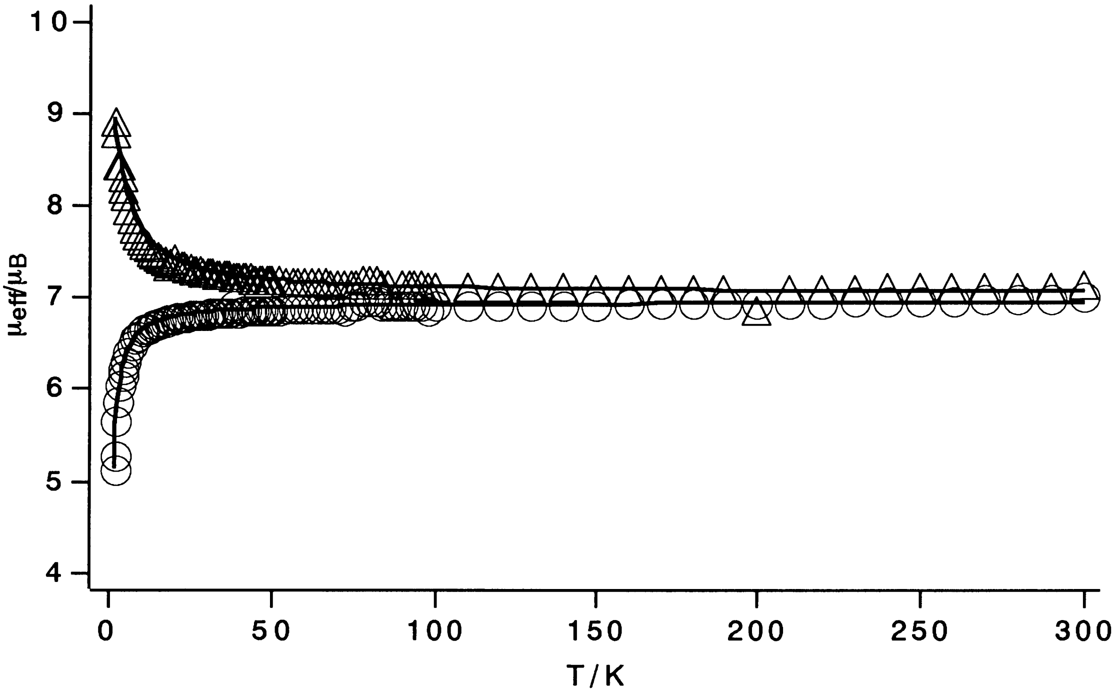


Fig. 2. Temperature dependence of the effective magnetic moment ($\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$) of Mn(hfac)$_2$/**4-NOIm** (Δ) and Mn(hfac)$_2$/**3-NOIm** (O). Solid curves represent the theoretical best-fit curves in accordance with eq 1.

where g is assumed to be 2, f is a purity factor, and all other symbols have their usual meaning. Fitting of eq 1 to the observed $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ vs. T plots for the two Mn(II) complexes by means of a least-squares method gave $2J/k_B = +1.18 \pm 0.58$ K and $f = 1.03$ for Mn(hfac)$_2$/**4-NOIm** and $2J/k_B = -0.448 \pm 0.004$ K and $f = 1.001$ for Mn(hfac)$_2$/**3-NOIm**. The best fit curves are also given by solid curves in Fig. 2.

It is concluded that the two manganese(II) centers joined together through two (1-imidazolyl)phenyl nitroxide groups interacted to each other weakly ($|2J/k_B| < 2$ K) and the signs of the exchange interaction depended on the position of the nitroxide radicals on the phenyl ring, positive ($2J/k_B = 1.18$ K) for 4- and negative (- 0.45 K) for 3-position of the phenyl ring. The latter value is quite small in magnitude and contribution of other factors such as through-space antiferromagnetic interaction between the manganese ions may not be excluded although separated by 10.65 and 7.54 Å within and between the dimer molecules. We still can say that the sign of the exchange interaction is different in these two complexes which have molecular structure very similar to each other. The regiospecificity is interpreted in terms of the polarization of the π-electron spins which is well established in organic π-diradicals[2)] but not necessarily so in heterospin systems consisting of 3d-transition metals and organic radicals.[9)] Previously, we showed similar regiospecificity in the sign of the exchange coupling in a pair of pyridylnitroxides as the sixth axial ligands in metalloporphyrin systems.[10] The effective role of the π-spin polarization in the regiospecificity in these metal-radical coupling and the present metal-radical-metal coupling promises positively the construction of extended hybrid-type high-spin complexes.

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5) $Mn(hfac)_2$/**3-NOIm**: Anal. Found: C, 39.42; H, 2.62; N, 6.09%. Calcd for $C_{23}H_{18}N_3O_5F_{12}Mn$: C, 39.50; H, 2.60; N, 6.01%. $Mn(hfac)_2$/**4-NOIm**: Found: C, 39.26; H, 2.78; N, 5.92%.

6) $Mn(hfac)_2$/**3-NOIm** crystallizes in the monoclinic space group $C2/c$ (#15), with a = 25.982(3) Å, b = 12.170(3) Å, c = 19.184(3) Å, b = 109.67(1)°, V = 5712(2) Å^3, Z = 4, and D_{calc} =1.629 g/cm^3. A crystal of $Mn(hfac)_2$/**4-NOIm** is the monoclinic space group $P2_1/n$ (#14), with a = 12.547(4) Å, b = 17.291(4) Å, c = 12.876(4) Å, β = 94.06(3)°, V = 2786(1) Å^3, Z = 2, and D_{calc} =1.667 g/cm^3. The structures were solved by direct methods and converged with full-matrix least-squares using the TEXSAN Version 2.0 program (Molecular Structure Corp.). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C-H 0.96 Å, C-C-H 109.5°, 120°, or 180°) and refined isotropically using a rigid model. Refinements converged at R = 0.068, R_w = 0.059 for 3982 unique refrections with $I > 3\sigma(I)$ and 417 variables for $Mn(hfac)_2$/**3-NOIm** and at R = 0.061, R_w = 0.060 for 5122 unique refrections with $I > 3\sigma(I)$ and 397 variables for $Mn(hfac)_2$/**4-NOIm**, respectively.

7) Estimated to be $2J/k_B$ = -200 - -400 K.[8]

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