Ferro- and Ferrimagnetic Ordering in a Two-Dimensional Network Formed by Manganese(II) and 1,3,5-Tris[*p*-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]benzene

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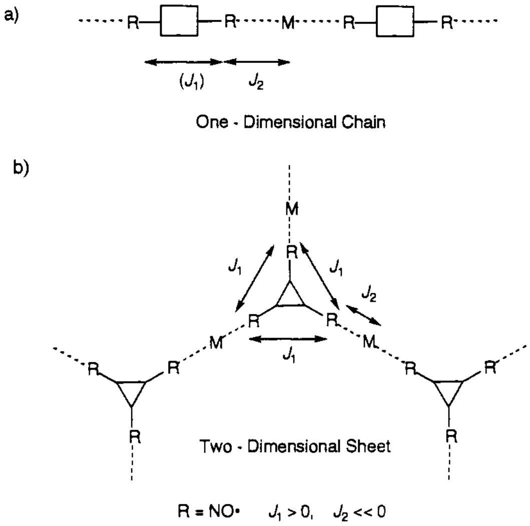
The search for molecular-based materials with relevant magnetic properties is a scientific subject of increasing interest.[1] Together with assemblies of entirely 3d spins of metal complexes and those of 2p spins of purely organic radicals, the heterospin systems consisting of transition-metal ions and organic free radicals as ligands constitute one of the mainstreams of such studies.[2,3] The ligands employed are often organic monoradicals that have two ligating sites, e.g., semiquinones[3] and nitronylnitroxides,[2] and, as a result, the magnetic materials have one-dimensional (1-D) spin structures (Chart 1a). The interaction between the 1-D chains is weaker compared with the intrachain interaction, and the critical temperatures (T_c) for undergoing the transition to ferro- and/or ferrimagnets are consequently very low.[3] If 2-D and 3-D networks are formed by the metal and the ligating organic radicals, T_c may then be very high, as discussed by Kahn.[4] $V(TCNE)_2 \cdot {}^1/_2CH_2Cl_2$ with T_c above 300 K may be such an example.[5]

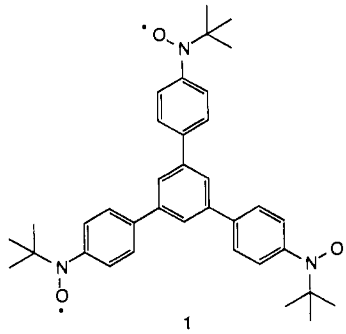
In order to expand dimensionality, we have introduced a new strategy of employing π-conjugated polynitroxides as the ligands that have more than two ligating sites and ferromagnetic intramolecular couplings ($J_1 > 0$) (Chart 1b). A result on a thus fabricated two-dimensional spin network composed of trinitroxide radical **1** having a quartet ground state (J_1/k_B = 6.8 K)[6] and manganese(II) hexafluoroacetylacetonate (hfac) is reported here.

The complex $\mathbf{1}_2 \cdot [Mn(II)(hfac)_2]_3 \cdot n\text{-}C_7H_{16}$ was obtained by dissolving 100 mg (19.8 mmol) of $Mn(II)(hfac)_2 \cdot 2H_2O$ in a mixture of 1 mL of diethyl ether, 10 mL of *n*-heptane, and 10 mL of benzene followed by addition of 82.1 mg (13.2 mmol) of **1**[6] in 5 mL of benzene. Black blocks were formed from the deep violet solution.

Chart 1



The X-ray crystal structure of the complex[7] revealed that the Mn(II) ion has an octahedral coordination with four equatorial oxygen atoms of two hfac anions and two axial oxygen atoms of two nitroxide groups from different molecules of **1**. Six triradical molecules and six Mn ions make an expanded hexagon from which an extended honeycomb network is constructed by sharing its edges (Figure 1). A disordered *n*-heptane molecule is contained in each hexagonal cavity.[7] The 2-D network sheets form a graphite-like layered structure in which the mean interlayer distance is 3.58 Å and the adjacent layers are slid in the *ab* plane by a length of the edge of the hexagon from the superimposable disposition. As a result, any middle benzene ring of **1** stacks with the corresponding ring on the next layer rotated by 60° along the C_3 axis. On the basis of the spin density and interatomic distance, the strongest interlayer exchange interaction is found between the outer benzene ring carbon of **1** para to the nitroxide group on one layer and the meta carbons on the next layer at a distance of 3.78 Å. This type of interaction is expected to be ferromagnetic, as dictated by McConnell theory.[8]



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The temperature dependence of the molar magnetic susceptibility χ per $\mathbf{1}_2 \cdot [Mn(II)(hfac)_2]_3$ unit was investigated at several magnetic fields.[9] A typical data at 5000 Oe expressed in the form of the χT versus T plot (Figure 2, inset) gave a minimum at ca. 115 K. The observed μ_{eff} value $[(3k\chi T/N)^{1/2}]$ of 6.7 μ_B at this temperature is in good agreement with a model in which the interaction between the Mn(II) and the nitroxide group directly attached to it is antiferromagnetic and the three spins within molecules of **1** are not yet ordered. The χT value then increased with decreasing temperature and showed a maximum at 2.5 K. When the measurement was carried out in a much lower field of 1 Oe, the magnetization values showed a sharp rise

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(1) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Ferromagnetic and High Spin Molecular Based Materials. Miller, J. S., Dougherty, D. A., Eds. *Mol. Cryst. Liq. Cryst.* **1989**, *176*. (c) Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. Eds.; *Magnetic Molecular Materials*; NATO ASI Series E; Kluwer Academic Publishers: Dordrecht, 1991. (d) Chemistry and Physics of Molecular Based Magnetic Materials. Iwamura, H., Miller, J. S., Eds. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, *233*.

(2) Caneschi, A.; Gatteschi, D.; Rey, P. *Prog. Inorg. Chem.* **1991**, 331. Caneschi, A.; Gatteschi, D.; Sessoli, R. In ref 1c, p 215.

(3) Benelli, C.; Dei, A.; Gatteschi, D.; Gudel, H. U.; Pardi, L. *Inorg. Chem.* **1989**, *28*, 3089.

(4) Stumpf, H. O.; Pei, Yu.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 6738. Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447.

(5) Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415.

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(7) Crystal data for $\mathbf{1}_2 \cdot Mn(II)_3 \cdot (hfac)_6 \cdot n\text{-}C_7H_{16}$: $C_{102}H_{90}N_6O_{18}F_{36}\text{-}Mn_3 \cdot C_7H_{16}$, M = 2636.82, rhombohedral (hexagonal axes), space group $R\bar{3}$-(*h*) (No. 148), a = 28.462(7) Å, c = 18.40(1) Å, V = 12914(8) Å^3, Z = 4, and D_X = 1.356 g/cm^3; crystal dimensions 0.30 × 0.40 × 0.20 mm^3 in a glass capillary (the crystals effloresced by releasing *n*-heptane in the air). Rigaku AFC-5R diffractometer of this department, μ(Mo Kα) = 3.84 cm^{-1}; 2θ(max) = 55.1° at 22 °C; 1435 unique reflections with $I > 3\sigma(I)$ and 258 variables. Non-hydrogen atoms were refined anisotropically except for those of the disordered *n*-heptane molecules, R = 0.090 and R_w = 0.112. The disorder and the fragility of the crystals made it difficult to improve the quality of the analysis.

(8) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(9) Application of Curie–Weiss law to the temperature dependence of χ gave C = 7.16 emu K mol^{-1} and θ = −44.2 K in the range 180–300 K and C = 5.60 emu K mol^{-1} and θ = +1.8 K in the range 30–100 K.

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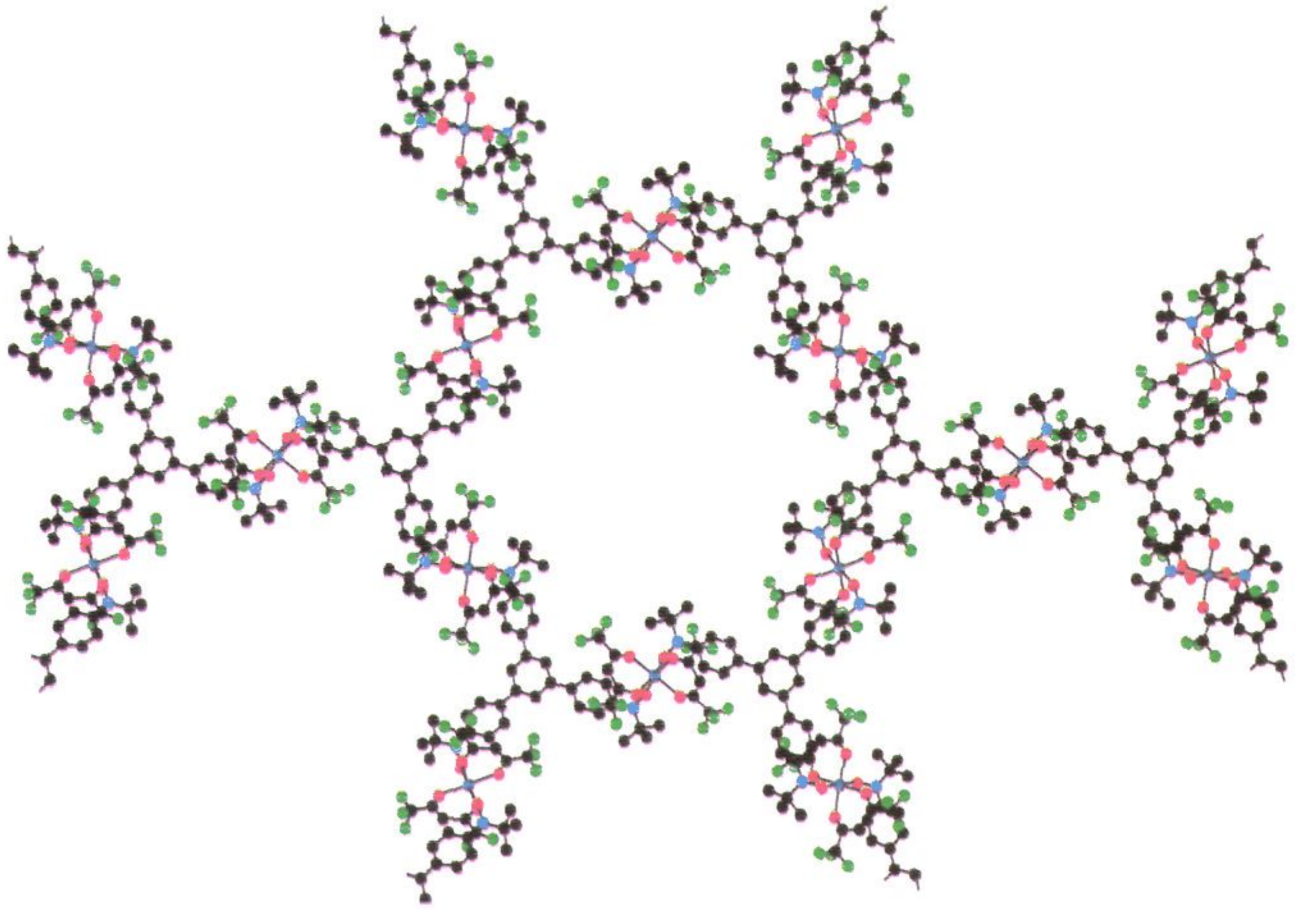

Figure 1. View along the c axis of a layer showing the hexagons made of six trinitroxide radical **1** and six manganese complexes Mn(II)(hfac)$_2$. The Mn(II) ions (each bonded to six oxygens) are represented in deep blue, the oxygen atoms in red, the nitrogen atoms in blue, the carbon atoms in black, and the fluorine atoms in green. The included n-heptane molecules are not shown for clarity.

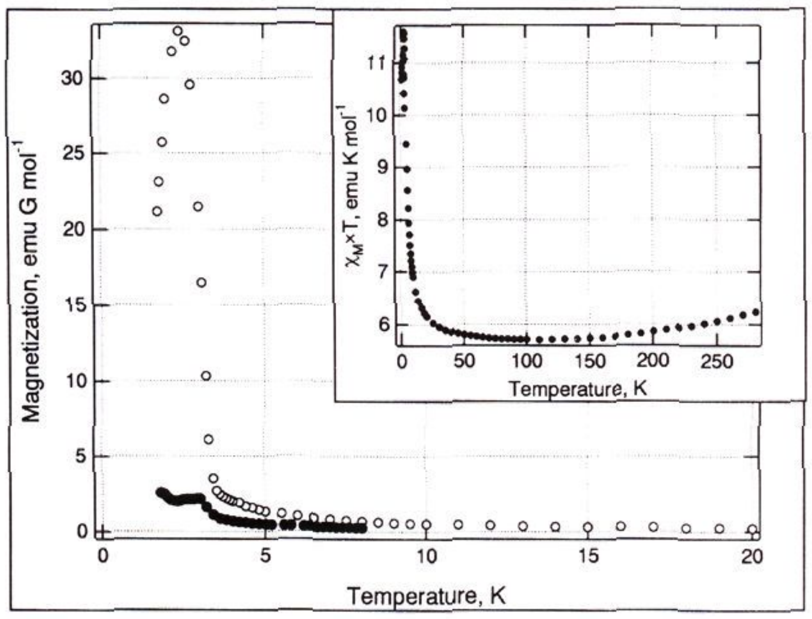

Figure 2. Observed magnetization versus T plots for the complex $\mathbf{1}_2\cdot$[Mn(II)(hfac)$_2$]$_3$ measured at a magnetic field of 1 Oe (○) and spontaneous magnetization (●). The inset shows the χT versus T plots for the complex measured at 5000 Oe.

at T_c = 3.4 K (Figure 2). The spontaneous magnetization was observed below T_c, demonstrating the transition to a bulk magnet. The magnetization value of the complex below T_c decreased at lower temperature, probably due to the immobilization of the domain walls.[10] When the field dependence of the magnetization was measured at 1.8 K, the magnetization reached to ca. 9 μ_B at 30 000 Oe and became saturated (Figure 3). The antiferromagnetic interaction between the Mn(II) and **1** ($J_2 < 0$ in Chart 1b) would predict the saturated magnetization value of 9 μ_B ($5/2 \times 3 - 3/2 \times 2 = 9/2$), in good agreement with the observed value. A hysteresis loop (the remnant magnetization of 53.9 emu G mol^{-1} and the coercive field of 3.8 Oe) was observed at 2 K.

It is concluded that the perfect 2-D ferrimagnetic sheets withheterospin ferromagnetic ($J_1 > 0$) – antiferromagnetic ($J_2 < 0$ in Chart 1b) network together with ferromagnetic stacking of the layers have been realized. The observed T_c to the ferro/ferrimagnet was not so high as expected from the layered 2-D structure. This result is explicable by the fact that the T_c value to the magnet in these systems depends on the strength of the intramolecular interaction (J_1) within the nitroxide molecule **1**, which is only 6.8k_BK. Other polynitroxides that are expected to have stronger ferromagnetic interactions are being tested as ligands for similar complexes in these laboratories.

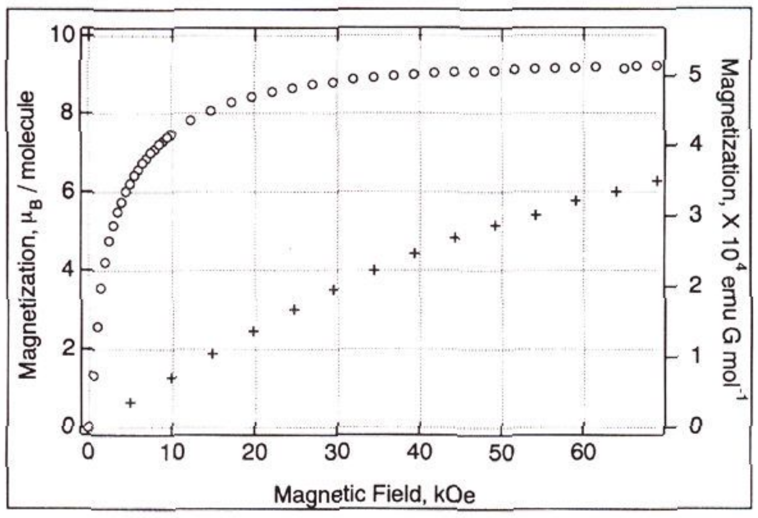

Figure 3. Field dependence of the magnetization measured at 1.8 K (○) and 10.8 K (+).

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Supplementary Material Available: Listing of crystallographic data and processing descriptions, final atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and PLUTO and ORTEP drawings for the complex $\mathbf{1}_2\cdot$[Mn(II)(hfac)$_2$]$_3\cdot n$-C$_7$H$_{16}$ (25 pages); tables of observed and calculated structure factors (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Unoriented microcrystalline samples were used. For similar phenomena, see: Hitzfeld, M.; Ziemann, P.; Buckel, W.; Claus, H. *Phys. Rev. B* **1984**, *29*, 5023. Kahn, O. In *Organic and Inorganic Low-Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum: New York, 1987; p 93. Contribution of an additional magnetic transition below T_c cannot be excluded at the present stage and is a subject of further study.