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Assemblage and Alignment of the Spins of the Organic Trinitroxide Radical with a Quartet Ground State by Means of Complexation with Magnetic Metal Ions. A Molecule-Based Magnet with Three-Dimensional Structure and High T_C of 46 K

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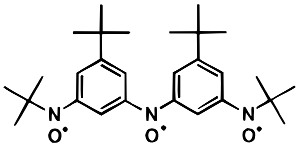
When a molecule is endowed with two electrons for two degenerate or nearly degenerate orthogonal orbitals, the Coulombic repulsion between the two electrons will be minimized by allocating one electron to each orbtial with parallel spins, as dictated by Hund's rule. On the basis of this and extended principles, quite a few organic molecules with high-spin ground states have been prepared.[1] Some of the highlights include a nonacarbene with 18 parallel spins ($S = 9$), characterized at cryogenic temperature,[2] and triradicals with three parallel spins ($S = {}^3/_2$),[3] among which trinitroxide radical **1**[3a] is noted for its high stability at room temperature under air. Efforts to increase the number of the aligned spins have, however, been hampered by the development of antiferromagnetic intra- and/or interchain interactions between the radical and/or carbene centers assembled in high local concentration; chemical bonds appear to be formed in the extreme.[4]



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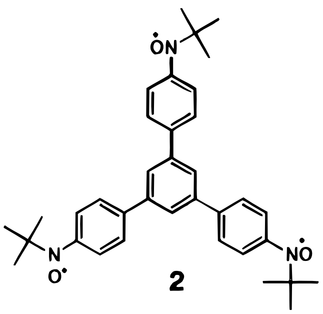

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To overcome these difficulties, we have made recourse to a strategy of assembling the organic radical centers by means of complexation with paramagnetic transition metal ions.[5] When bis(hexafluoroacetylacetonato)manganese(II) [Mn(II)(hfac)$_2$] was treated with a highly symmetric trinitroxide radical **2**,[3b] the expected 3:2 complex with a two-dimensional honeycomb-shaped network structure was obtained. The complex became a magnet with a transition temperature (T_C) from the paramagnetic to the ferro-/ferrimagnetically spin-ordered phase of 3.4 K.[6] While the strategy proved to be effective, the low T_C was ascribed to the weak intramolecular exchange coupling ($J_{intra} = 6.8$ K)[6] of **2**. We have therefore studied complexes of **1**, which has a much stronger J_{intra} value of 240 K.[3a]

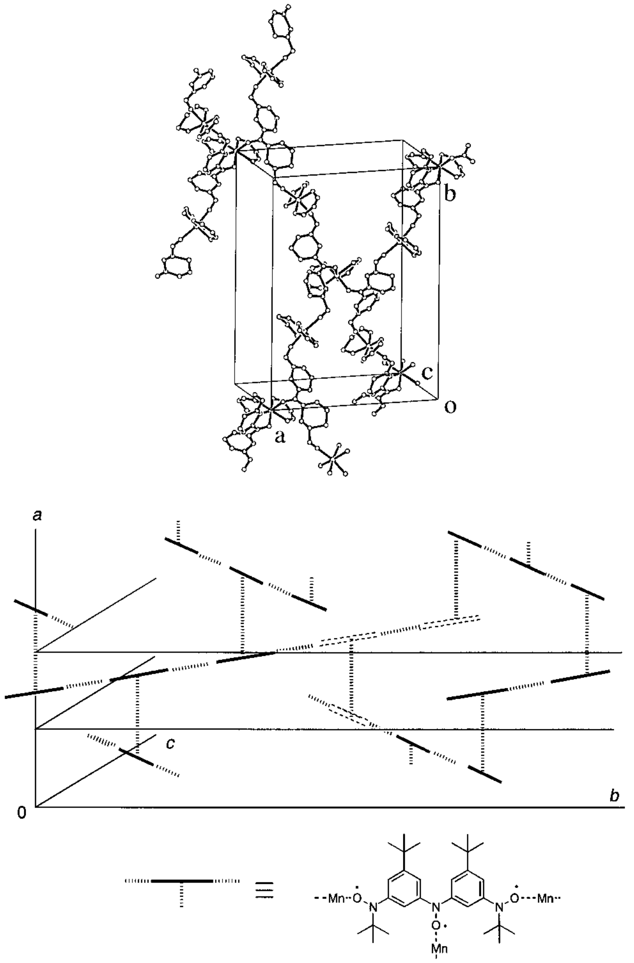

Figure 1. Packing of the polymer complex $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$ (a, top) projected along [001] (the CF_3 and *tert*-butyl groups are not shown for clarity) and (b, bottom) viewed schematically to show the 3-D parallel crosses motif.

Triradical **1** was mixed with 1.73 molar excess of dehydrated Mn(hfac)$_2$ in *n*-heptane, diethyl ether, and a small amount of chloroform. A stream of argon was passed over the solution, and black precipitates of $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$ were obtained at 0 °C in 10 days. Crystals of this complex obtained in 31% yield are stable at room temperature in the air for more than a year.

An X-ray structure analysis of an orthorhombic crystal of the complex revealed the formation of a parallel crosses-shaped

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(5) Precedents for the idea of assembling organic monoradicals with paramagnetic transition metal ions are found in the following: Caneschi, A.; Gatteschi, D.; Rey, P. *Prog. Inorg. Chem.* **1991**, *39*, 331. Some of the highest T_C values ever reported are 22.5 K for Mn(II)Cu(II) monoradical (Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447) and 34 K for Co(II)Cu(II) monoradical (Stumpf, H. O.; Pei, Y.; Michaut, C.; Kahn, O.; Renard, J. P.; Ouahab, L. *Chem. Mater.* **1994**, *6*, 257). V(TCNE)$_2$·nCH$_2$Cl$_2$, with T_C above 300 K with unknown crystal structure, may also belong to this family of complexes (Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415).

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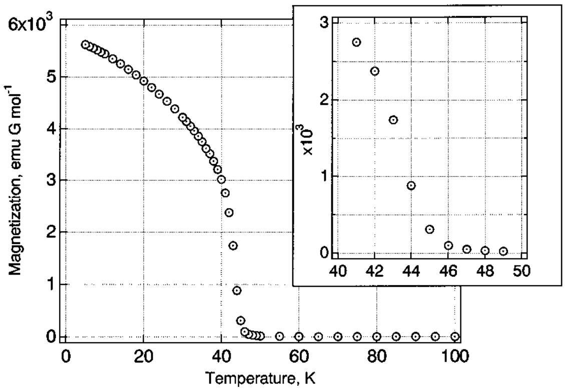

Figure 2. Temperature dependence of magnetization at a field of 5 Oe of a polycrystalline sample of $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$. See inset for the temperature range 40−50 K.

three-dimensional polymeric network (Figure 1).[7] Two oxygen atoms, one from each terminal nitroxide group of triradical **1**, are ligated to two different manganese ions to form a one-dimensional chain extending in the (0,+1,+1) or (1,+1,−1) direction of the crystal lattice. Since any manganese ion in an octahedral position at the corner of the crystal lattice is attached to the two nitroxide oxygens from two different triradical molecules in a *trans* disposition, the trinitroxide molecules are in zigzag orientation along the chain. The diphenyl nitroxide unit in **1** assumes a chiral C_2 conformation, and the resulting chain is syndiotactic in that *R* and *S* enantiomers alternate along the chain. A third Mn(II) ion in an octahedral position in the middle of the crystal lattice is used to link in a *cis* configuration the middle nitroxide groups of the two ligand molecules of **1** of the same chirality from two adjacent chains. The intersecting angle of the parallel crosses is estimated to be ~60°.

The temperature dependence of the molar magnetic susceptibility χ_{mol} was investigated at a field of 5000 Oe. A $\chi_{mol}T$ value of 8.64 emu K mol^{-1} at 300 K is larger than the theoretical value of 5.63 emu K mol^{-1} expected for a short-range antiferromagnetic ordering of six $^1/_2$ spins of **1** and three $^5/_2$ spins of d^2 Mn(II) for $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$. As the temperature is lowered, the χ_{mol} T value did not develop any minimum characteristic of the short-range ordering of the spins by antiferromagnetic interaction but instead increased monotonically, reflecting the increase in the correlation length within the network. Strong antiferromagnetic coupling ($J_{inter} < -300$ K) between the Mn(II) ion and the nitroxide radical of **1** and the onset of the intramolecular ferromagnetic coupling (J_{intra}) among the three nitroxide radicals in the latter at room temperature are also suggested.

The temperature dependence of the magnetization *M* for a polycrystalline sample of $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$ was investigated at 5 Oe. When the sample was cooled within the field of 5 Oe, the field-cooled magnetization showed an abrupt rise at $T_C = 46$ K (Figure 2). The field dependence of the magnetization at 5 K showed two important features. First, the magnetization rose sharply at low field, reached a value of ~9 μ_B (50 000 emu G mol^{-1}) at 220 Oe, and became saturated (Figure 3a). The saturation value is in good agreement with a theoretical one of 9 μ_B ($^5/_2 \times 3 - {}^3/_2 \times 2 = {}^9/_2$) expected for the antiferromagnetic ordering between the d^5 Mn(II) ion and $S = {}^3/_2$ triradical **1**. Second, a conspicuous magnetocrystalline anisotropy was found in which the easy axis of magnetization lies along the *a* axis of the crystal lattice and the hard axis lies perpendicular to it (Figure 3).

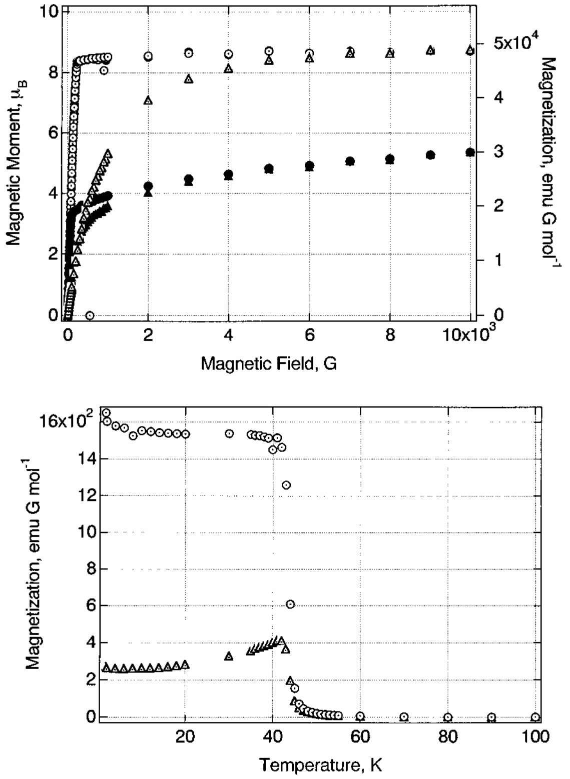

Figure 3. (a, top) Field dependencies of the magnetic moment at 5 (open symbols) and 40 K (closed symbols) and (b, bottom) temperature dependencies of the magnetization at 5 Oe of the oriented sample of $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$. The applied field is parallel (circles) and perpendicular (triangles) to the *a* axis.

It is concluded that a perfect 3-D ferro-/ferrimagnet with ferromagnetic ($J_{intra} > 0$) and antiferromagnetic ($J_{inter} < 0$) networks is realized in $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$.

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Supporting Information Available: Listing of crystallographic data and processing descriptions for the crystal structure of complex $\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2$ (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(7) A black block single crystal of $[\{Mn(hfac)_2\}_3\cdot\mathbf{1}_2]$ in approximate dimensions of 0.60 mm × 0.80 mm × 0.80 mm was mounted in a glass capillary. Diffraction data were obtained with $2\theta(\max) = 55.1°$ at 22 °C. The structure was solved in *Pnn*2 (No. 34) to give crystal data: $Mn_3F_{36}O_{18}N_6C_{86}H_{90}$, MW = 2344.44, orthorhombic, space group *Pnn*2 (No. 34), $a = 17.82(1)$ Å, $b = 24.367(4)$ Å, $c = 12.522(2)$ Å, $V = 5436(4)$ Å^3, and $D_X = 1.432$ g/cm^3 for $Z = 2$. Nonhydrogen atoms were refined anisotropically and isotropically. Refinement converged at $R = 0.180$ and $R_w = 0.108$ for 2960 unique reflections, with $I > 4\sigma(I)$ and 590 variables. Difficulty in the reduction of the residuals lies in the disorder of the CF_3 and *tert*-butyl groups. Refinement is still in progress.