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High-Spin Polynitroxide Radicals as Versatile Bridging Ligands for High Tc Transition Metal Complexes

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HIGH-SPIN POLYNITROXIDE RADICALS AS VERSATILE BRIDGING LIGANDS FOR HIGH T_C TRANSITION METAL COMPLEXES

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Abstract Organic di- and trinitroxide radicals with triplet and quartet ground states, respectively, were allowed to react with manganese(II) bis(hexafluoroacetylacetonate) to give polymer complexes having well-defined dimensionality. While 1:1 1-D complex from the *m*-phenylenebis(nitroxide) was found to be a metamagnet (T_C = 5.5 K), 2:3 2-D complexes from the trinitroxides became ferri/ferromagnets with T_C in the range 3.4 - 46 K, demonstrating the merit of these hetero-spin systems as a design strategy for molecule-based magnets.

INTRODUCTION

Construction of molecular based magnetic materials that have well-defined one- or two-dimensional structures is a scientific subject of increasing interest.[1] Heterospin systems consisting of transition metal ions and organic free radicals as ligands constitute one of the mainstreams of such studies. Several of these materials have been established to have finite critical temperatures for undergoing transition to ferro- and/or ferrimagnets.[2] The ligands employed are often organic monoradicals that have two ligating sites, e.g., semiquinones[3] and Ullman's nitronyl nitroxides.[2] They are represented schematically as shown in Figure 1a.

We wish to introduce a new strategy of employing π-conjugated polynitroxides as bridging ligands in which the spins of the unpaired electrons interact ferromagnetically {J(intraligand) > 0}.[4] The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighboring spins may be readily tuned in this strategy. A bis(monodentate) diradical with a triplet ground state (S = 1) would form in all probability a 1:1

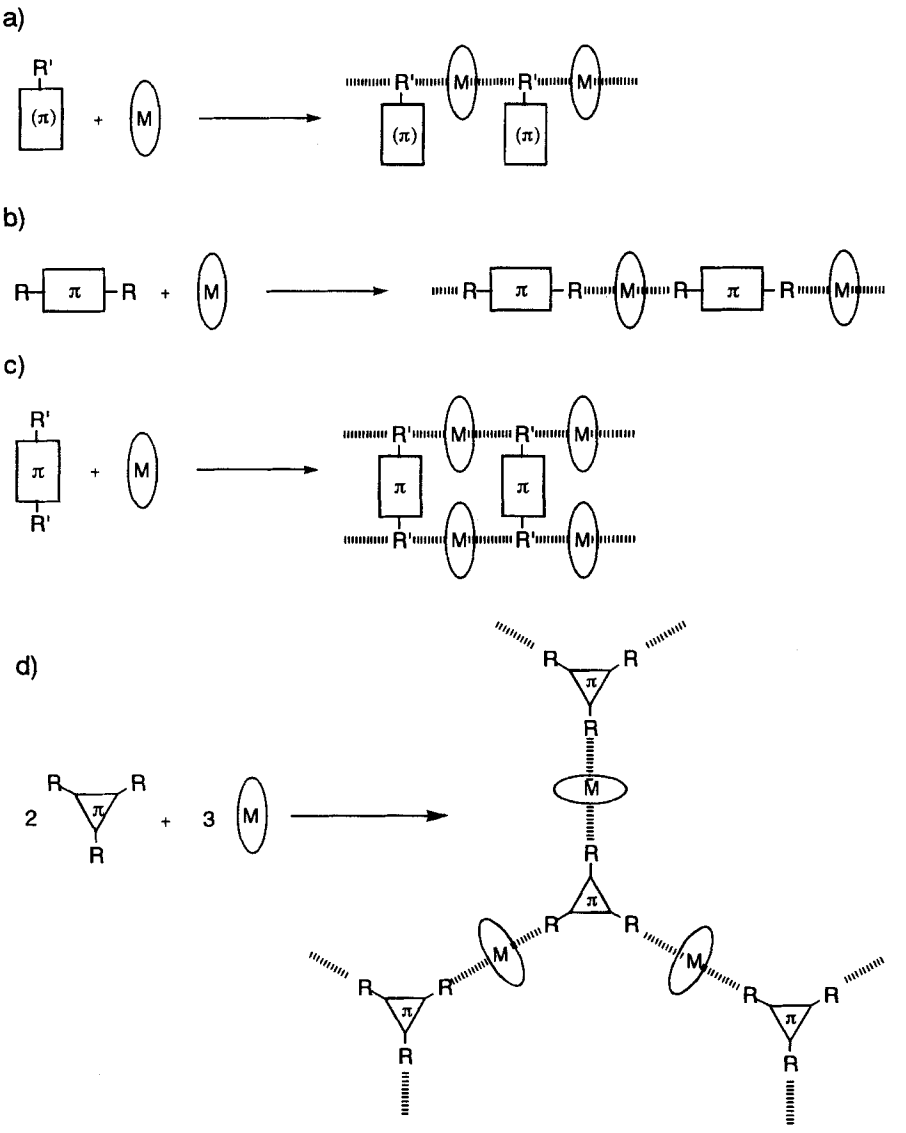


FIGURE 1 Schematic drawings of the formation of a) 1-D chains or macrocycles from bis(monodentate) monoradicals and b) triplet diradicals, c) ladder polymers from triplet bis{bis(monodentate)} diradicals, and d) 2-D network sheets from tris(monodentate) quartet triradicals, all with 3d transition metal ions M.

complex consisting of a one-dimensional chain (Figure 1b).[5] Since the exchange coupling between the ligands and the directly attached 3d metal ions is typically antiferromagnetic {J(coordination) << 0}, the residual spin would be established for the repeating unit unless the spin of the latter is unity. Such a one-dimensional (1-D) array of spins would become an antiferro-, meta-,[5] or ferromagnet depending on the nature of the interchain interaction. Since the interaction between the 1-D chains is much weaker compared with the intrachain interaction, the critical temperatures (T_C) for undergoing the magnetic transition will consequently be very low. For a triplet diradical such as a bis(semiquinone) and a bis(nitronyl nitroxide) in which each radical center can serve as a bis(monodentate) bridging ligand, complexation would give rise to a ladder polymer as in Figure 1c.[6] The spin ordering in such systems should be less vulnerable to defects than in purely one-dimensional systems.[1f,4] A tris(monodentate) triradical with a quartet ground state (S = 3/2) in which the radical centers are arranged in a triangular disposition would form a 2:3 complex with a coordinatively doubly unsaturated 3d metal ions M. In an ideal case, a hexagonal network structure would be generated (Figure 1d).[4] The spin alignment in these systems would be very much stabilized and is expected to give high T_C magnets. We wish to report here the preparation and characterization of thus fabricated one- and two-dimensional magnets composed of bis- and trisnitroxide radicals on the one hand and 3d transition metal complexes, e.g., manganese(II) bis(hexafluoroacetyl-acetonate), Mn(II)(hfac)$_2$, on the other.

PREPARATION OF THE 3d TRANSITION METAL - POLYNITROXIDE RADICAL COMPLEXES

Di- and Trinitroxide Radicals

Di- and trinitroxide radicals having radical centers joined through π-conjugated ferromagnetic coupling units, e.g., *m*-phenylene and 1,3,5-benzenetriyl, were prepared by lithiation of the polybromo compounds followed by reaction with 2-methyl-2-nitrosopropane. When the metal-halogen exchange reaction was not complete, the resulting hydroxyamines were protected by O-silylation with *tert*-butylchlorodimethylsilane in the presence of imidazole. After a second metal-halogen exchange and reaction with the nitroso compound, deprotection was effected by the reaction with

tetra-*n*-butyl-ammonium fluoride. The poly(hydroxyamine)s thus obtained were treated with Ag_2O in ether to give the solutions containing the corresponding polynitroxide radicals. Some polyradicals were prone to polymerization when concentrated to dryness; they were kept in solution and used for analytical and other measurements and preparation of the metal complexes right after the preparation. Radicals **1**,[7] **2**,[7d] and **5**[7c] have already been reported.

Aromatic dialdehydes were condensed with 2,3-bis(hydroxyamino)-2,3-dimethylbutane and the resulting imidazolidines were treated with PbO_2 to give the corresponding bis(Ullman's nitronyl nitroxide)s.[6]

Metal Complexes

The complex **1**•Mn(II)(hfac)$_2$ was obtained by dissolving 61.0 mg (0.12 mmol) of Mn(hfac)$_2$•2H$_2$O in a mixture of 1 ml of acetone and 10 ml of *n*-heptane to which were added 30.0 mg (0.12 mmol) of **1**[7] in 10 ml of *n*-heptane. The solution was concentrated under reduced pressure to ca. 5 ml to give black needles from a deep brown solution.[5]

The complex **2**$_2$•[Mn(II)(hfac)$_2$]$_3$•*n*-C$_7$H$_{16}$ was obtained by dissolving 100 mg (0.198 mmol) of Mn(II)(hfac)$_2$•2H$_2$O in a mixture of 1 ml of diethyl ether, 10 ml *n*-heptane and 10 ml of benzene followed by addition of 82.1 mg (0.132 mmol) of **2**[8] in 5 ml of benzene. Black blocks were formed from a deep violet solution.[4]

While trinitroxides **3** and **5** gave similar 2:3 complexes with Mn(hfac)$_2$, **4** did not form any complex probably due to steric congestion around the ligand molecule. Thiophene-2,4-bis(Ullman's nitronyl nitroxide) **6** gave with Mn(II)(hfac)$_2$ dark green powders of complex **6**$_2$•[Mn(II)(hfac)$_2$]$_3$•CH$_2$Cl$_2$. The expected 1:2 complex was not obtained.[6]

FERROMAGNETIC INTRAMOLECULAR COUPLING IN THE POLYNITROXIDE RADICAL LIGANDS

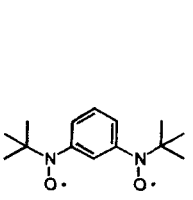
The magnitude of the exchange coupling between the nitroxide radicals in the ligands before the complex formation was studied by means of the temperature dependence of their effective magnetic moments.

The energy gaps of the high-spin ground states and the low-spin excited states (singlets for the diradicals and doubly degenerate doublets for the triradicals) are summarized in Table 1. Temperature dependence of the

effective magnetic moments of **3** isolated in a PVC film was measured on a SQUID susceptometer and analyzed in terms of an isosceles triangular three spin system.[7d]

TABLE I. The magnitude of the exchange coupling between the nitroxide radicals in di- and trinitroxide radicals **1** ~**6**.

nitroxide radical	J_{intra}, K	θ, K	sample morphology	ref
1	≥ 300	-7.8	crystals	5
2	+6.8 ± 0.1	-2.13 ± 0.04	crystals	8
2	+5.3 ± 0.1		isolated in Tween 40	8
3	~300, +67 ± 5		isolated in PVC	
4	≥ 300		crystals	7d
5	+240 ± 20	-19 ± 2	crystals	7c
6	+80 ± 4	-0.04 ± 0.02	crystals	6



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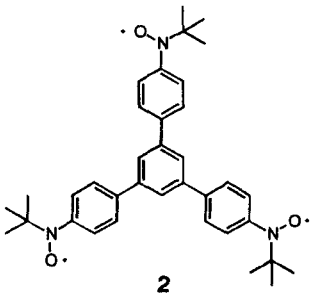

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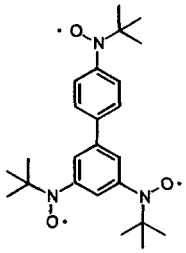

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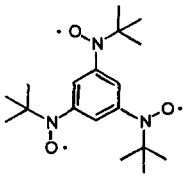

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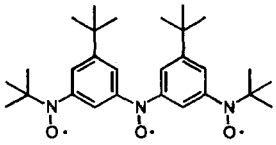

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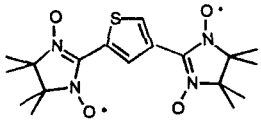

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X-RAY CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPLEXES

Crystal data of the manganese complexes of nitroxides **1** and **2** are collected

in Table 2. The X-ray crystal structure of the complex **1**•Mn(II)(hfac)$_2$ revealed that the manganese(II) ion has an octahedral coordination with the four oxygen atoms of two hfac anions and the two oxygen atoms of the two nitroxide groups from two different dinitroxide molecules of **1**. The latters are bound to the Mn(II) ion in *cis*-configuration. As a result, the Mn ion and the diradical molecules form an alternating zigzag one-dimensional polymeric chain structure (Figure 2).[5] The strongest interchain coupling is found in the N(tert-Bu)O• --- F --- N(tert-Bu)O• interaction with the distances of 4.95 Å on the one hand and 4.97 Å on the other. This type of interaction is suggested to be antiferromagnetic as dictated by the McConnell's theory[9a] and the super-exchange mechanism through the fluorine atom.

TABLE II. Crystallographic data for the manganese(II) complexes **1**•Mn(II)(hfac)$_2$[5] and **2**$_2$•[Mn(II)(hfac)$_2$]$_3$•*n*-C$_7$H$_{16}$.[4]

chemical formula	$C_{24}H_{24}N_2O_6F_{12}Mn$	$C_{102}H_{90}N_6O_{18}F_{36}Mn_3$•$C_7H_{16}$
a, Å	9.212(3)	28.462(7)
b, Å	16.620(3)	
c, Å	20.088(2)	18.40(1)
β		98.46(1) °
V, Å^3	3042(1)	12914 (8)
Z	4	4
formula weight	719.38	2636.82
space group	$P2_1/n$ (No. 14)	R3(h) (No. 148)
T, °C	21	22
λ, Å	0.71069	0.71069
ρ_{calc}, g cm^{-1}	1.571	1.356
$R(F_o)$	0.055	0.090
$R_W(F_o)$	0.058	0.112

The Mn(II) ion in complex **2**$_2$•[Mn(II)(hfac)$_2$]$_3$•*n*-C$_7$H$_{16}$ 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 **2**. Six triradical molecules and six Mn ions make an expanded hexagon from

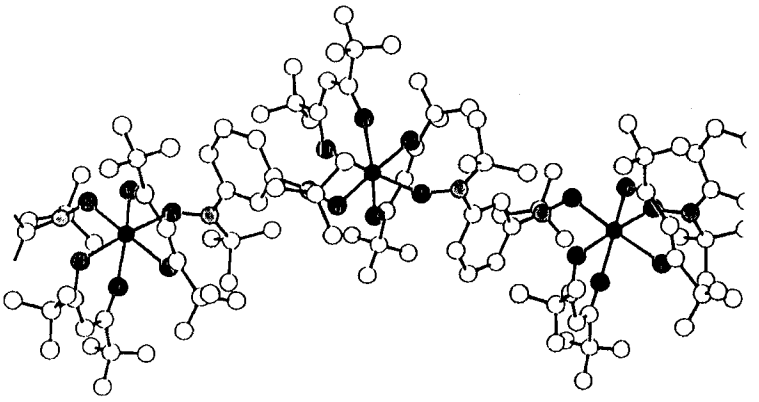

FIGURE 2 View of a 1-D chain formed by bisnitroxide **1** and Mn(II)(hfac)$_2$. The Mn(II) ions are represented in black, the oxygen atoms in gray, the nitrogen atoms in shaded, and the carbon and fluorine atoms in open circles.

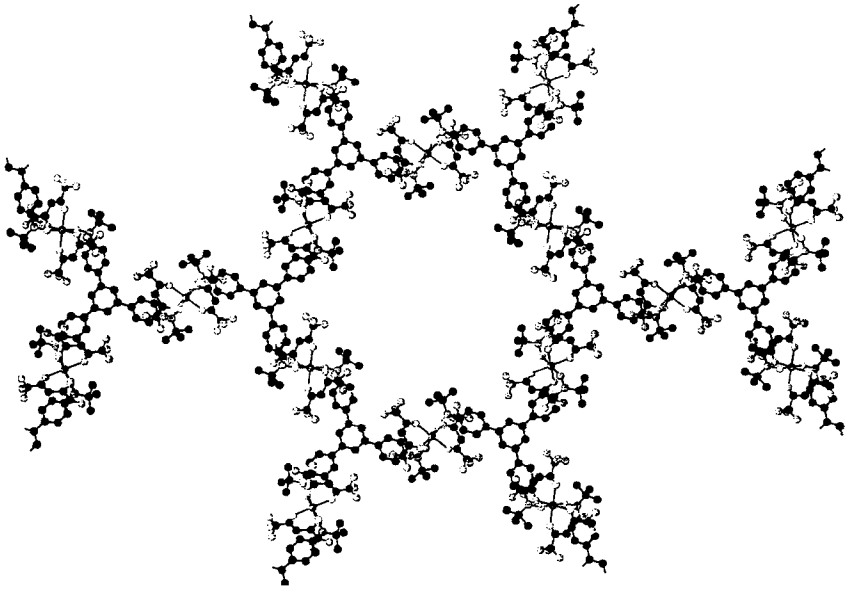

FIGURE 3 View along the *c* axis of a layer showing the hexagons made of six molecules of trinitroxide radical **2** and six Mn(II)(hfac)$_2$ complexes.

which an extended honey-comb network is constructed by sharing its edges (Figure 3). A disordered *n*-heptane molecule is contained in each hexagonal cavity.[4] The two-dimensional 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 **2** stacks with the corresponding ring on the next layer rotated by 60° along the C_3 axis. On the basis of the spin density, phase of the π-electron polarization, and interatomic distance, the strongest ferromagnetic interlayer exchange interaction[9] is found between the outer benzene ring carbon of **2** para to the nitroxide group on one layer and the meta carbon on the next layer at a distance of 3.78 Å.

A preliminary result on the structural analysis of **5**$_2$•[Mn(II)(hfac)$_2$]$_3$ has revealed that the two terminal nitroxide oxygens of **5** are coordinated with two different manganese ions to make a linear chain as in **1**•Mn(II)(hfac)$_2$. The nitroxide radical in the middle of the molecule appears to be used to cross-link the neighboring chains to make a higher dimensional structure. Neither **3**$_2$•[Mn(II)(hfac)$_2$]$_3$ nor **6**$_2$•[Mn(II)(hfac)$_2$]$_3$•CH_2Cl_2 gave good single crystals amenable to X-ray crystal structure analysis.

MAGNETIC PROPERTIES

1:1 Complex **1**•Mn(II)(hfac)$_2$ consisting of a 1-D chain (Figure 1b)

The temperature dependence of the molar magnetic susceptibility χ for **1**•Mn(II)(hfac)$_2$ was investigated at several magnetic field strengths. In the magnetic field of 5000 Oe, the product χT of the molar susceptibility and temperature increased steadily with decreasing temperature, reached a maximum at 8.5 K, and then decreased (Figure 4 (Inset)). The observed χT value of 2.11 emu K mol^{-1} at 300 K is slightly but not much larger than the theoretical value of 1.88 emu K mol^{-1} for a model in which the interaction between the Mn(II) and the directly attached nitroxide radical is antiferromagnetic and the two spins within the molecule of **1** are not yet ordered. Application of Curie-Weiss law to the temperature dependence of χ gave a Curie constant C of 1.9 emu K mol^{-1} and a Weiss constant θ of 40 K in the range 50-350 K. When the measurement was carried out in a much lower field, the magnetic susceptibility value showed a sharp rise at 5.5 K and then decreased with decreasing temperature (Figure 4). The ZFC magnetization shows also a sharp cusp at 5.5 K. The magnetization at 1.8 K revealed metamagnetic behavior. Namely, while the response of the magnetization was not sensitive to the weak applied magnetic field below ca. 200 Oe, a

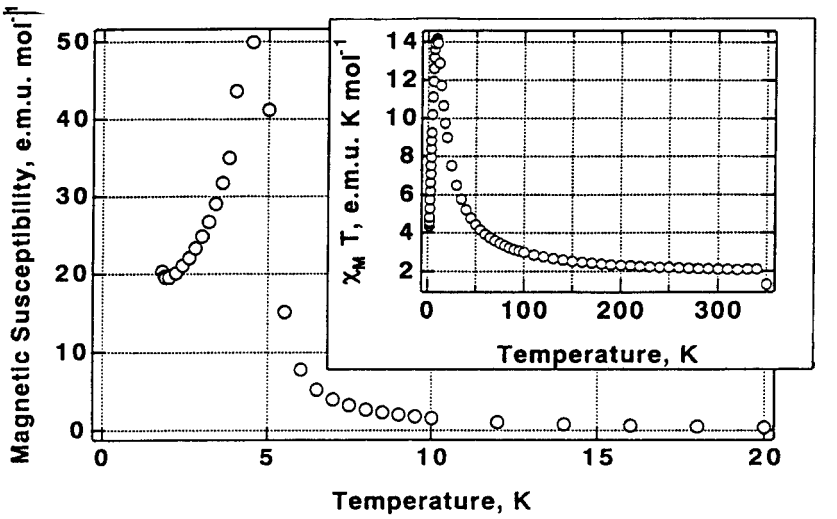

FIGURE 4 Molar magnetic susceptibility χ_M vs. T plots for the complex **1**•Mn(II)(hfac)$_2$ measured at 1 Oe. Similar plots for the complex measured at 5000 Oe are given in Inset.

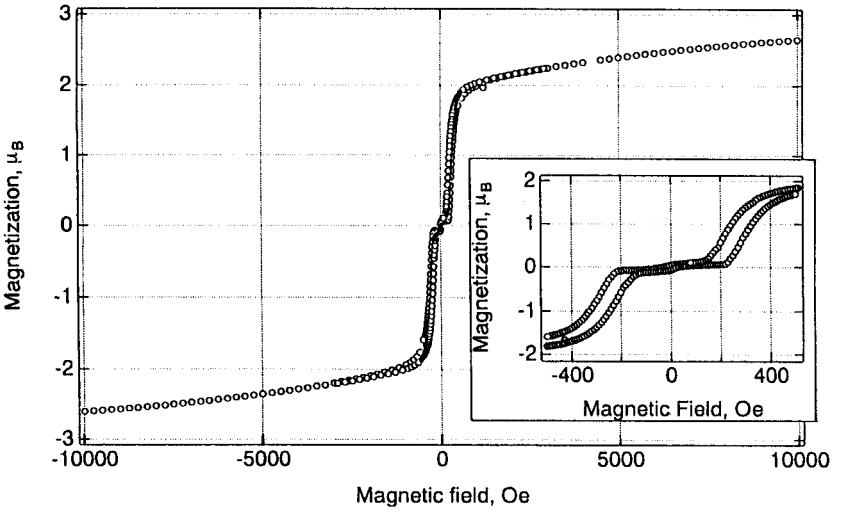

FIGURE 5 Field dependence of the magnetization of **1**•Mn(II)(hfac)$_2$ measured at 1.8 K.

behavior characteristic of an antiferromagnet, a sharp rise and approach to saturation of magnetization characteristic of a ferromagnet was observed at higher applied magnetic field (Figure 5 (Inset)). A saturation magnetization value of ca. 3 μ_B was reached at 1.8 K at 30 000 Oe (Figure 5). When the interaction between the manganese(II) ion and **1** is antiferromagnetic (J_{coord}

< 0), the value of M_{sat} for **1**•Mn(II)(hfac)$_2$ is expect to be 3 μ_B (5/2 - 2/2 = 3/2) in good agreement with the observed value.

The 1-D hybrid-chain consisting of ferromagnetic ($J_{intra} > 0$) and antiferromagnetic ($J_{coord} < 0$) couplings has been established. Any meaningful interchain interaction is estimated to be due to the antiferromagnetic superexchange between the two nitroxide centers on the adjacent chains through the fluorine atom (vide supra). The complex undergoes transition to a metamagnet at 5.5 K;[5,10] below this temperature it behaves as an antiferromagnet, but the magnetization increases sharply and becomes readily saturated at the field higher than 200 Oe.

2:3 Complex **2**$_2$•[Mn(II)(hfac)$_2$]$_3$ and its with 2-D network structure (Figure 1d)

The temperature dependence of the molar magnetic susceptibility χ per **2**$_2$•[Mn(II)(hfac)$_2$]$_3$ unit was investigated at several magnetic fields.[4] A typical data at 5000 Oe expressed in the form of the χT versus T plot (Figure 6, 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 a molecules of **2** are not yet ordered. Then the χT value increased with decreasing temperature and showed a maximum at 2.5 K. When the measurement was carried out in much lower field of 1 Oe, the magnetization values showed a sharp rise at T_C = 3.4 K (Figure 6). 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.[11] When the field dependence of the magnetization was measured at 1.8 K, the magnetization reached to ca. 9 μ_B at 30000 Oe and became saturated. The antiferromagnetic interaction between the Mn(II) and **2** ($J_{coord} < 0$) would predict a saturated magnetization value of 9 μ_B (5/2 × 3 - 3/2 × 2 = 9/2) in good agreement with the observed value. A hysteresis loop at 2 K consisted of the remnant magnetization of 53.9 emu G mol^{-1} and the coercive field of 3.8 Oe.

While the perfect 2-D network sheets with ferro- ($J_{intra} > 0$) and antiferromagnetic ($J_{coord} < 0$) coupling together with ferromagnetic stacking of the layers have been obtained, the observed T_C to the ferro/ferrimagnet was not so high as expected from such a high-dimensional structure. The result is

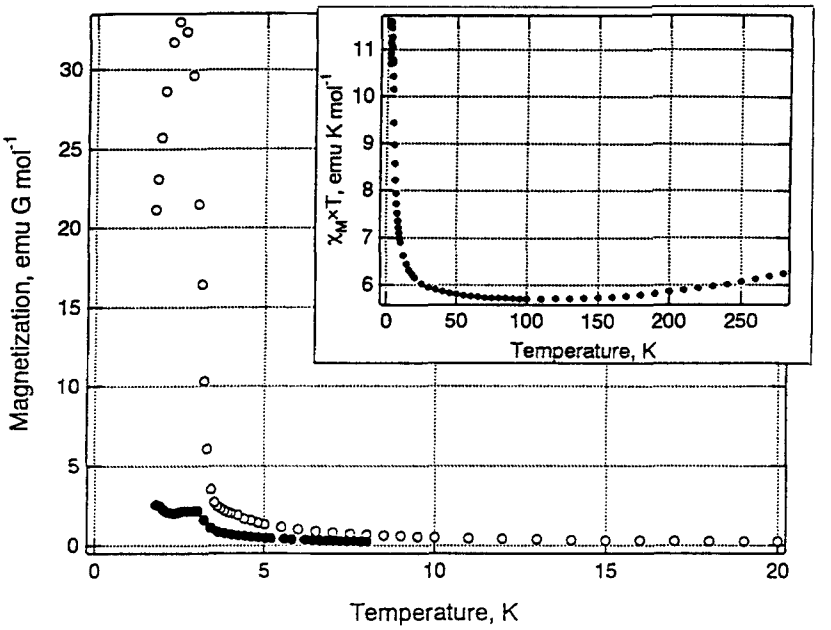

FIGURE 6 Observed magnetization vs. T plots for the complex $\mathbf{2}_2$•[Mn(II)(hfac)$_2$]$_3$ measured at a magnetic field of 1 Oe (○) and spontaneous magnetization (•). The inset shows the χT vs. T plots for the complex measured at 5000 Oe.

ascribed to the weak (J_{intra} = 6.8 K) intramolecular coupling among the three nitroxide units in the molecule of **2**. Any triradical that has three nitroxide groups arranged in a triangular fashion with a larger J_{intra} value should have a higher T_C value. Trinitroxides **3** and **4** that have stronger ferromagnetic interactions (see Table 1) have therefore been tested. The T_C value increased to 9.3 K indeed in black blocks of $\mathbf{3}_2$•[Mn(II)(hfac)$_2$]$_3$.[12] Unfortunately, **4** did not afford any complex with Mn(II)(hfac)$_2$.

2:3 Complex $\mathbf{6}_2$•[Mn(II)(hfac)$_2$]$_3$•CH_2Cl_2 with a potential ladder polymer structure (Figure 1c)

The $\chi_g T$ value for dark green powders of $\mathbf{6}_2$•[Mn(II)(hfac)$_2$]$_3$•CH_2Cl_2 was 6.85× 10^{-3} emu K g^{-1} at 300 K at a field of 100 mT. This value corresponding to 15.7 emu K mol^{-1} agrees in the order of magnitude with a paramagnetic sample of S = 4/2, a theoretical value (5/2 - 1/2) for the antiferromagnetic short-range interaction between the d^5 Mn ion and the nitroxide radical in this complex. As the temperature was lowered, the $\chi_g T$ values remained constant,

began to increase gradually at 140 K and steeply at 12.5 K, and then decreased below 10 K at fields of 100 and 0.5 mT. The field-cooled magnetization (FCM) measured upon cooling down within the field showed a rapid increase of M with a change of sign for the second derivative at 11 K.[6] When the sample was cooled down within the field and then warmed up in zero field, a remnant magnetization (REM) was observed, which vanished at 11 K. These data clearly indicate that the sample behaved as a magnet with a spontaneous magnetization below 11 K. When the field dependence of the magnetization was studied in fields of 0-7 T below 11 K, it is noted that the M values increased steeply to ca. 10 emu G g^{-1} in the range 0 - 30 mT, and then gradually at 30 mT and above. At 1.8 K, a hysteresis loop with remnant magnetization of 5.3 emu G g^{-1} and coercive force of 2.2 mT was observed.

In place of a linear chain or a macrocycle (Figure 1a) made of 2-substituted nitronyl nitroxide with $Mn(hfac)_2$,[3] formation of a ladder polymer (Figure 1c)[1f] or other structures in higher dimension had been expected. The obtained complexes are still deficient in the metal ions. While the transition to a magnet was confirmed to take place at 11 K, the observed magnetization curve which consisted of the extremely field-sensitive and slowly saturating parts suggested that not all but ca. 30% of the unpaired electrons in this powder sample take part in the spontaneous alignment below the critical temperature. The rest of the spins appear to be independent or form less ordered segments. This is not unreasonable as the radical sites are not fully ligated with the manganese ions.

Complex $\mathbf{5}_2$•$[Mn(II)(hfac)_2]_3$ with highest T_C of 46 K

The field-cooled magnetization (FCM) of complex $\mathbf{5}_2$•$[Mn(II)(hfac)_2]_3$ at a field of 5 Oe showed a rapid increase of M at 46 K.[13] The zero-field-cooled magnetization (ZFCM) showed the freezing temperature T_f of 43 K (Figure 7). The remnant magnetization (REM) vanished at 46 K. While the X-ray structural analysis is too preliminary to conclude if the cross-linking of the 1-D chains by means of the middle nitroxide group of **5** is two- or three-dimensional, the presence of the deformed network structure corresponding to Figure 1d has been confirmed.

CONCLUSION

Assemblage and ordering of the unpaired electrons of high-spin polynitroxide

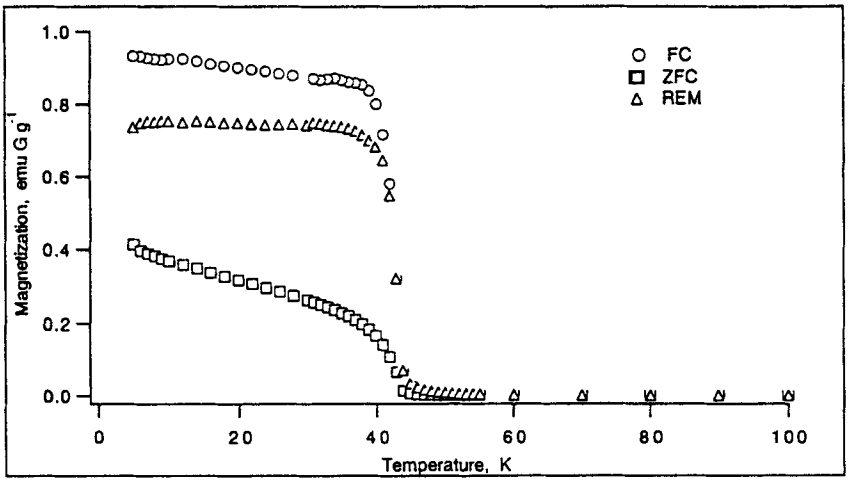

FIGURE 7 Observed temperature dependence of magnetization for $\mathbf{5}_2$•[Mn(II)(hfac)$_2$]$_3$ at a field of 5 Oe.

radicals in macroscopic scale have been effectively achieved by means of coordination with paramagnetic 3d transition metal ions. These heterospin systems promise to serve as a strong design strategy for high T_C molecule-based magnetic materials. While the 1-D and 2-D structures have now been reasonably well established, construction of well-designed 3-D structures remain to be explored systematically as discussed by Kahn *et al.*[14] and as suggested to be instrumental in developing T_C above 300 K in V(TCNE)$_2$•*n*CH$_2$Cl$_2$.[15]

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