

High-spin polynitroxide radicals as versatile bridging ligands for transition metal complexes with high ferri/ferromagnetic T_C

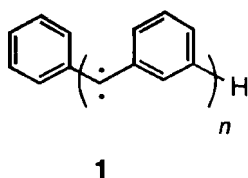
Hiizu Iwamura, Katsuya Inoue,[†] and Takashi Hayamizu

Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-81, and [†]Department of Chemistry, Kitasato University, 1-5-1 Kitasato, Sagami-hara, Kanagawa 228, Japan

Abstract: π -Conjugated 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 structures. While a 1:1 1-D complex from the *m*-phenylenebis(nitroxide) **5** was found to be a metamagnet ($T_C = 5.5$ K), 2:3 2-D and 3-D complexes from the trinitroxides **7–9** became ferri/ferromagnets with T_C in the range 3.4–46 K. Design of these self-assembled heterospin systems with tailored dimensions and the sign and magnitude of the exchange coupling will serve as a useful strategy for exploring higher T_C molecule-based magnets.

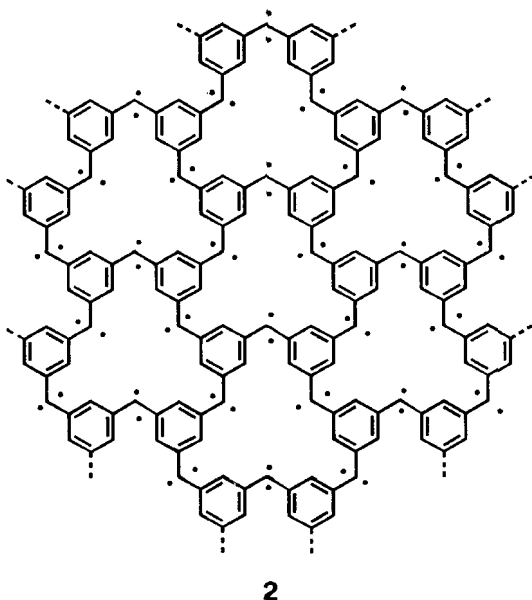
INTRODUCTION

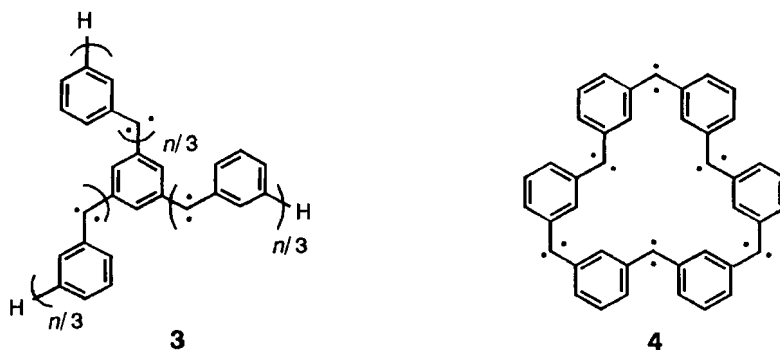
At the 5th International Symposium on Novel Aromatic Compounds in St. Andrews, we presented a paper demonstrating that all eight electron spins of tetracarbene **1** ($n = 4$) are aligned in parallel in its ground state and therefore polycarbene **1** constitutes a prototype of one-dimensional organic ferromagnets (1). The system has since been extended to a higher homolog **1** ($n = 5$)(2). The spin alignment is based on two structural features: orthogonality of the singly occupied orbitals at the carbene center and topological symmetry of the *m*-phenylene diradicals (3). Since the one-dimensional spin alignment cannot in principle afford the spontaneous magnetization at finite temperature and is vulnerable to chemical defects in practice (4), two-dimensional network structure **2** has then been employed as a long-range goal. While some constituent units **3** and **4** contained in **2** have been synthesized and proved to be the highest-spin



hydrocarbons ($S = 6$ and 9 for **3** ($n = 6$ and 9 , respectively)) ever obtained (5), intermolecular interactions between the polycarbene molecules were found to be mostly antiferromagnetic and polymer network itself **2** remained to be synthesized.

Some coordinatively doubly unsaturated magnetic metal complexes and organic free radicals carrying two ligating sites, e.g., semiquinones and Ullman's nitronyl nitroxides, form one-dimensional chains or macrocycles that have finite temperatures for exhibiting spontaneous magnetization (6). They are represented schematically as shown in Fig. 1a.

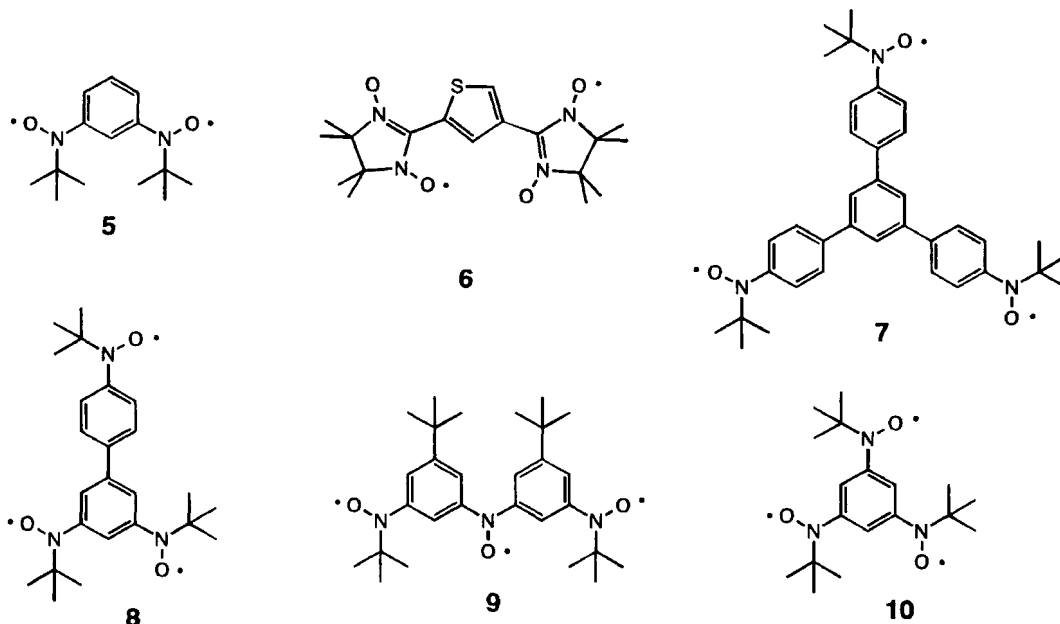




We have been very much inspired by these observations and decided to take advantage of the magnetic metal ions-promoted self-assemblage of organic free radicals to construct macroscopic spins.

STRATEGY FOR CONSTRUCTING TAILORED MAGNETIC STRUCTURES

π -Conjugated polynitroxides **5** - **10** have been employed as bridging ligands in which the spins of the unpaired electrons interact ferromagnetically $\{J(\text{intra-ligand}) > 0\}$. The dimension 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 ($S = 1$), e.g., **5**, would form a one-dimensional chain of 1:1 complex (Fig. 1b). Since the exchange coupling between the ligands and the directly attached d^5 metal ions is typically antiferromagnetic $\{J(\text{coordination}) \ll 0\}$, 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-, 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 such magnetic transitions will consequently be very low. For a triplet diradical such as bis(nitronyl nitroxide) **6** in which each radical center can serve as a bis(monodentate) bridging ligand, complexation would give rise to a ladder polymer as in Fig. 1c. The spin ordering in such a system should be less vulnerable to defects than in purely one-dimensional systems. Tris(monodentate) triradicals with quartet ground states ($S = 3/2$) in which the radical centers are arranged in a triangular disposition, e.g., **7**, **8** and **10**, would form 3:2 complexes with a coordinatively doubly unsaturated 3d metal ions M . In an ideal case, a hexagonal network structure would be generated (Fig. 1d). A quartet triradical carrying two unequivalent ligating sites, e.g., **9**, would form a 1-D chain by using two terminal nitroxide groups. The middle nitroxide group might then be used to interlink the chains to form a 2-D or 3-D network structure (Fig. 1e). The spin alignment in these systems would be very much stabilized and is expected to give high T_C magnets.



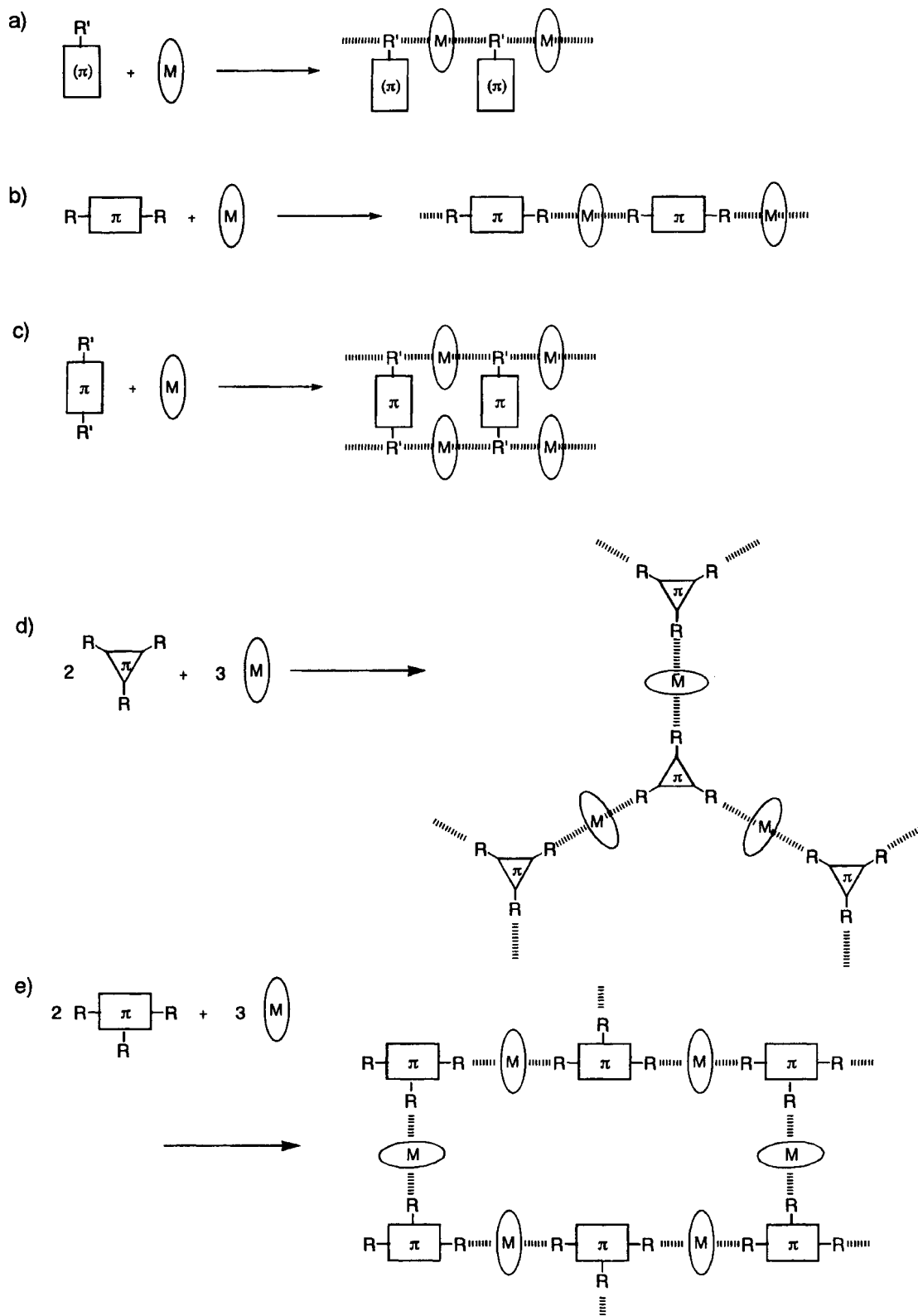


Fig. 1 Schematic drawings for the formation of a) 1-D chains or macrocycles from bis(monodentate) monoradicals and b) triplet diradicals, c) ladder polymers from triplet bis{bis(monodentate)} diradicals, d) 2-D network sheets from tris(monodentate) quartet triradicals, and e) 2-D networks/3-D crossed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

PREPARATION OF 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 hydroxylamines were protected by O-silylation. After a second metal-halogen exchange and reaction with the nitroso compound, deprotection was effected by tetra-*n*-butyl-ammonium fluoride. The poly(hydroxylamine)s thus obtained were treated with Ag₂O in ether to give the solutions containing the corresponding polynitroxide radicals. Some polyradicals were prone to polymerization when concentrated to dryness (7); they were kept in solution and used for analytical and other measurements and preparation of the metal complexes right after the preparation.

Thiophene-2,4-bis(carboxyaldehyde) was condensed with 2,3-bis(hydroxylamino)-2,3-dimethylbutane and the resulting dihydroimidazole derivative was treated with PbO₂ to give **6** (8).

Metal Complexes

The complex Mn(II)(hfac)₂·**5** was obtained by dissolving 61.0 mg (0.12 mmol) of manganese(II) bis(hexafluoroacetylacetonate) dihydrate, Mn(hfac)₂·2H₂O, 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 **5** 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 (11).

The complex [Mn(II)(hfac)₂]₃·**7**·2·*n*-C₇H₁₆ was obtained by dissolving 100 mg (0.198 mmol) of Mn(II)(hfac)₂·2H₂O 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 **7** in 5 ml of benzene (9). Black blocks were formed from a deep violet solution.

While similar 3:2 complexes were obtained from Mn(hfac)₂ with trinitroxides **8** and **9**, no complex was formed with **10** probably because of steric congestion around this ligand molecule. Thiophene-2,4-bis(Ullman's nitronyl nitroxide) **6** gave with Mn(II)(hfac)₂ dark green powders of complex [Mn(II)(hfac)₂]₃·**6**·2·CH₂Cl₂; the expected 2:1 complex was not obtained (8).

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 1. The magnitude of the exchange coupling between the nitroxide radicals in di- and trinitroxide radicals **5** - **10**

nitroxide radical	J_{intra} , K	θ , K	sample morphology	ref
5	≥ 300	-7.8	crystals	7a,b,c
6	$+80 \pm 4$	-0.04 ± 0.02	crystals	8
7	$+6.8 \pm 0.1$	-2.13 ± 0.04	crystals	7d
7	$+5.3 \pm 0.1$		isolated in Tween 40	7d
8	$\sim 300, +67 \pm 5^{(10)}$		isolated in PVC	14
9	$+240 \pm 20$	-19 ± 2	crystals	7c
10	≥ 300		crystals	7d

X-RAY CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPLEXES

Crystal data of the manganese complexes of nitroxides **5** and **7** are collected in TABLE 2.

1:1 Complex Mn(II)(hfac)₂·5 forming a 1-D chain

The X-ray crystal structure of the complex Mn(II)(hfac)₂·5 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 5 (11). The latter is bound to the Mn(II) ion in *cis*-configuration. It is noted that the resulting 1-D polymeric chain is isotactic in that the C₂ conformation of the molecules of 5 of the same chirality, i.e., R or S, is contained in a given chain (Fig. 2) (11). 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 (12) and the superexchange mechanism through the fluorine atom.

TABLE 2. Crystallographic data for the manganese(II) complexes Mn(II)(hfac)₂·5, [Mn(II)(hfac)₂]₃·7₂·*n*-C₇H₁₆ and [Mn(II)(hfac)₂]₃·9₂

chemical formula	C ₂₄ H ₂₄ N ₂ O ₆ F ₁₂ Mn	C ₁₀₂ H ₉₀ N ₆ O ₁₈ F ₃₆ Mn ₃ ·C ₇ H ₁₆	C ₈₆ H ₉₀ N ₆ O ₁₈ F ₃₆ Mn
<i>a</i> , Å	9.212(3)	28.462(7)	17.82(1)
<i>b</i> , Å	16.620(3)		24.367(4)
<i>c</i> , Å	20.088(2)	18.40(1)	12.522(2)
β		98.46(1) °	
<i>V</i> , Å ³	3042(1)	12914 (8)	5436(4)
<i>Z</i>	4	4	2
formula weight	719.38	2636.82	2344.44
space group	P2 ₁ /n (No. 14)	R3(h) (No. 148)	Pnn2(No.34)
<i>T</i> , °C	21	22	22
λ , Å	0.71069	0.71069	0.71069
ρ_{calc} , g cm ⁻³	1.571	1.356	1.432
<i>R</i> (F)	0.055	0.090	0.180
<i>R</i> w(F)	0.058	0.112	0.108

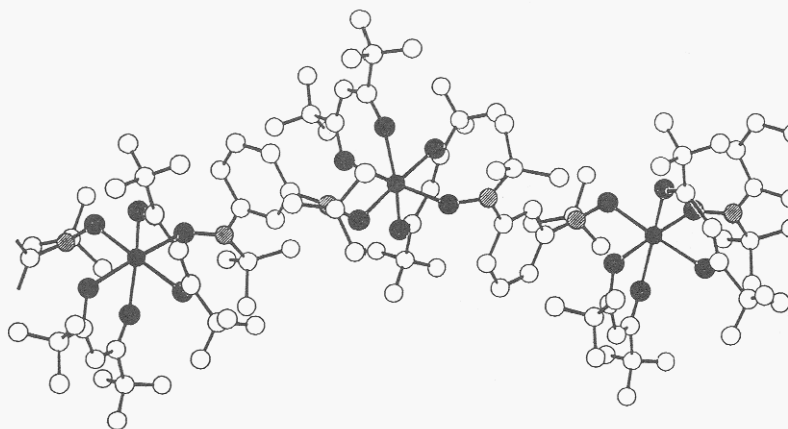


Fig. 2 View of a 1-D chain formed by bisnitroxide 5 and Mn(II)(hfac)₂ (11). The Mn(II) ions are represented in black, the oxygen atoms in gray, the nitrogen atoms in shaded, and the carbon and fluorine atoms in open circles.

3:2 Complex [Mn(II)(hfac)₂]₃·7₂ with 2-D network structure

The Mn(II) ion in complex [Mn(II)(hfac)₂]₃·7₂·*n*-C₇H₁₆ 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 7 (9). Six triradical molecules and six Mn ions make an expanded hexagon from which an extended honey-comb network is constructed by sharing its edges (Fig. 3). A disordered *n*-heptane molecule is contained in each hexagonal cavity. The two-dimensional network sheets form a

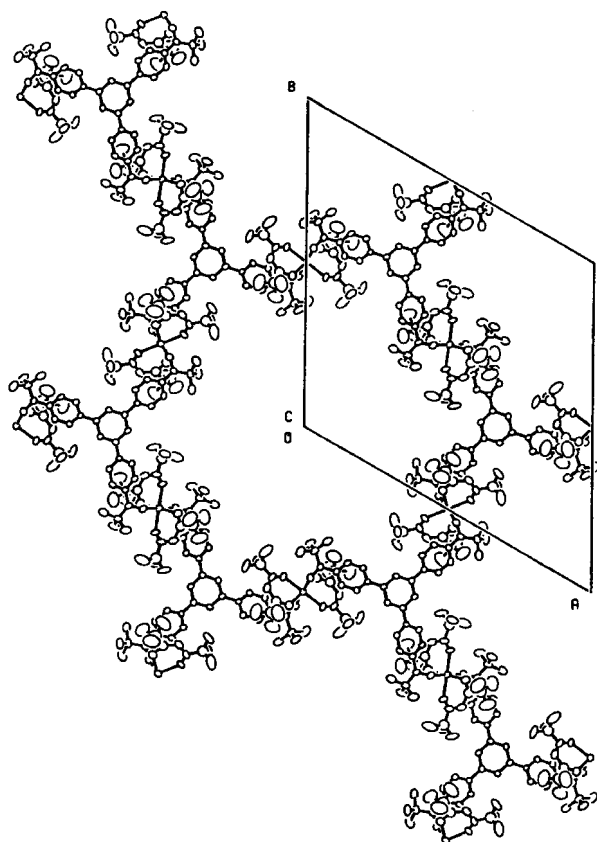


Fig. 3 View along the *c* axis of a layer showing the hexagons made of six molecules of trinitroxide radical **7** and six Mn(II)(hfac)_2 complexes (**9**).

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 **7** 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 (**12**) is found between the outer benzene ring carbon of **7** para to the nitroxide group on one layer and the meta carbon on the next layer at a distance of 3.78 Å.

3:2 Complex $[\text{Mn(II)(hfac)}_2]_3 \cdot \mathbf{9}_2$ with 3-D crossed parallels structure

A structural analysis of $[\text{Mn(II)(hfac)}_2]_3 \cdot \mathbf{9}_2$ has revealed that the two terminal nitroxide oxygens of **9** are coordinated with two different manganese ions to make a linear chain. In contrast to $\text{Mn(hfac)}_2 \cdot \mathbf{5}$ each Mn(II) is coordinated with two nitroxide oxygens in trans configuration and the resulting 1-D chain is syndiotactic in that the C_2 conformations of the molecules of **9** of opposite chirality alternate along the chain. The nitroxide radical in the middle of the molecule of **9** is used to cross-link the neighboring chains to make a 3-D structure with crossed parallels. The X-ray structure is schematically given in Fig. 4.

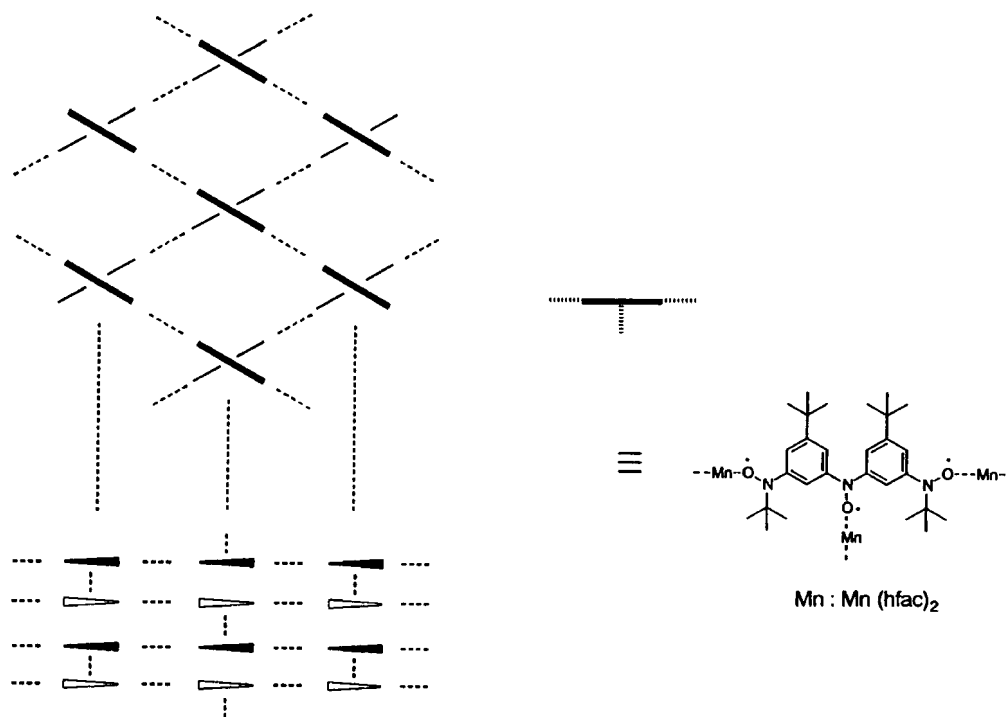


Fig. 4 Schematic drawing of the X-ray crossed-parallels structure of $[\text{Mn(II)(hfac)}_2]_3 \cdot \mathbf{9}_2$.

Neither $[\text{Mn}(\text{II})(\text{hfac})_2]_3 \cdot 6 \cdot \text{CH}_2\text{Cl}_2$ (8) nor $[\text{Mn}(\text{II})(\text{hfac})_2]_3 \cdot 8$ (14) gave good single crystals amenable to X-ray crystal structure analysis.

MAGNETIC PROPERTIES

Metamagnetic 1:1 complex $\text{Mn}(\text{II})(\text{hfac})_2 \cdot 5$

The temperature dependence of the molar magnetic susceptibility χ for $\text{Mn}(\text{II})(\text{hfac})_2 \cdot 5$ was investigated at several magnetic field strengths (11). 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. The observed χT value of $2.11 \text{ emu K mol}^{-1}$ at 300 K is slightly but not much larger than the theoretical value of $1.88 \text{ emu K mol}^{-1}$ for a model in which the interaction between the $\text{Mn}(\text{II})$ and the directly attached nitroxide radical is antiferro-magnetic and the two spins within the molecule of **5** are not yet ordered. Application of Curie-Weiss law to the temperature dependence of χ gave a Curie constant C of $1.9 \text{ emu K mol}^{-1}$ 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. 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,

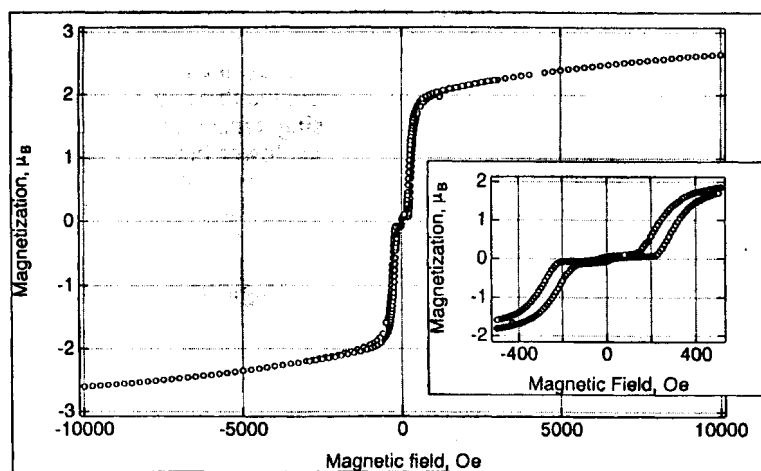


Fig. 5 Magnetization curves for the complex $\text{Mn}(\text{II})(\text{hfac})_2 \cdot 5$ measured at 1.8 K.

a 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 (Fig. 5). A saturation magnetization (M_{sat}) value of ca. $3 \mu\text{B}$ was reached at 1.8 K at 30 000 Oe. When the interaction between the manganese(II) ion and **5** is antiferromagnetic ($J_{\text{coord}} < 0$), the value of M_{sat} for $\text{Mn}(\text{II})(\text{hfac})_2 \cdot 5$ is expected to be $3 \mu\text{B}$ ($5/2 - 2/2 = 3/2$) in good agreement with the observed value.

The 1-D hybrid-chain consisting of ferromagnetic ($J_{\text{intra}} > 0$) and antiferromagnetic ($J_{\text{coord}} < 0$) couplings in $\text{Mn}(\text{II})(\text{hfac})_2 \cdot 5$ is similar to the magnetic structure of **1** in that each triplet carbene center ($S = 1$) of the latter is replaced with the antiferromagnetically coupled nitroxide-Mn(II)-nitroxide triad ($S = -1/2 + 5/2 - 1/2 = 3/2$). 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 (11); below this temperature it behaves as an antiferromagnet, but the magnetization increases sharply and becomes readily saturated at the field higher than 200 Oe.

3:2 Complex $[\text{Mn}(\text{II})(\text{hfac})_2]_3 \cdot 6 \cdot \text{CH}_2\text{Cl}_2$ with a potential ladder polymer structure and ferri/ferromagnetic T_C of 11 K

The $\chi_g T$ value for dark green powders of $[\text{Mn}(\text{II})(\text{hfac})_2]_3 \cdot 6 \cdot \text{CH}_2\text{Cl}_2$ was $6.85 \times 10^{-3} \text{ emu K g}^{-1}$ at 300 K at a field of 100 mT (8). This value corresponding to $15.7 \text{ emu K mol}^{-1}$ 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. 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⁻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.

Formation of a 2:1 ladder polymer (Fig. 1c) (15f) or other structures in higher dimension had been expected. The obtained complex was 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 magnetization 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.

3:2 Complex [Mn(II)(hfac)₂]₃·7₂ with ferri/ferromagnetic T_C of 3.4 K

The temperature dependence of the molar magnetic susceptibility χ per [Mn(II)(hfac)₂]₃·7₂ unit was investigated at several magnetic fields (9). A typical data at 5000 Oe expressed in the form of the χT versus T plot (Fig. 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 7 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 (Fig. 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 (16). 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. The antiferromagnetic interaction between the Mn(II) and 7 ($J_{\text{coord}} < 0$) would predict a M_{sat} 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 at 2 K consisted of the remnant magnetization of 53.9 emu G mol⁻¹ and the coercive field of 3.8 Oe.

The 2-D honey-comb network consisting of ferromagnetic ($J_{\text{intra}} > 0$) and antiferromagnetic ($J_{\text{coord}} < 0$) couplings in Mn(II)(hfac)₂·7 is similar to the magnetic structure of 2 in that each triplet carbene

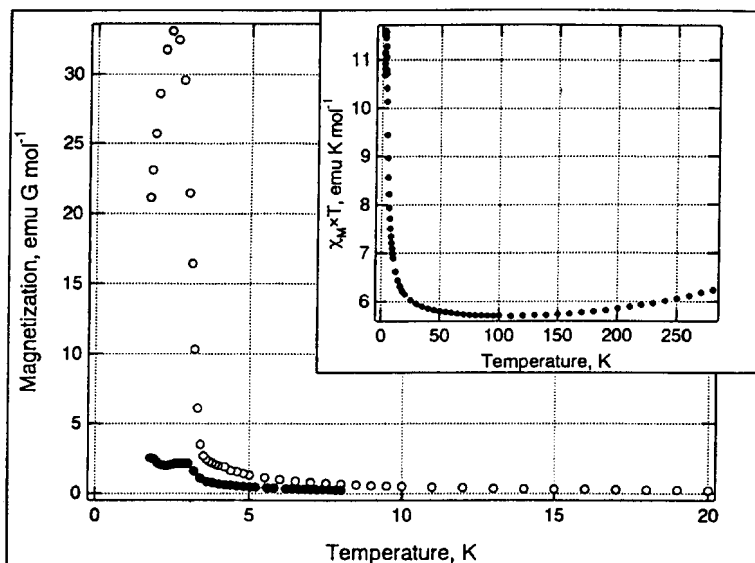


Fig. 6 Observed magnetization vs. T plots for the complex [Mn(II)(hfac)₂]₃·7₂ measured at a magnetic field of 1 Oe and spontaneous magnetization (9). The inset shows the χT vs. T plots for the complex measured at 5000 Oe.

center ($S = 1$) of the latter is replaced with the antiferromagnetically coupled nitroxide-Mn(II)-nitroxide triad ($S = -1/2 + 5/2 - 1/2 = 3/2$). In spite of this ferro- ($J_{\text{intra}} > 0$) and antiferromagnetically ($J_{\text{coord}} < 0$) coupled perfect 2-D network sheets together with ferromagnetic stacking of the layers in Mn(II)(hfac) $_2$ ·7, the observed T_C to the ferro/ferrimagnet was not so high as expected from such a high-dimensional structure. The result is ascribed to the weak ($J_{\text{intra}} = 6.8$ K) intramolecular coupling among the three nitroxide units in the molecule of 7 (7d). 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. Trinitroxide 8 that has stronger ferromagnetic interaction (see Table 1) has therefore been tested. The T_C value rose to 9.3 K indeed in black blocks of [Mn(II)(hfac) $_2$] $_3$ ·8 $_2$ (14).

3:2 Complex [Mn(II)(hfac) $_2$] $_3$ ·9 $_2$ with highest T_C of 46 K ever obtained

The field-cooled magnetization (FCM) of complex [Mn(II)(hfac) $_2$] $_3$ ·9 $_2$ at a field of 5 Oe showed a rapid increase of M at 46 K (Fig. 7). The zero-field-cooled magnetization (ZFCM) showed the freezing temperature T_f of 43 K. The remnant magnetization (REM) vanished at 46 K. 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. Secondly, conspicuous magnetocrystalline anisotropy was found in which the easy axis of magnetization lay along the a axis of the crystal lattice and the hard axis lay perpendicular to it. The 3-D magnetic structure was confirmed.

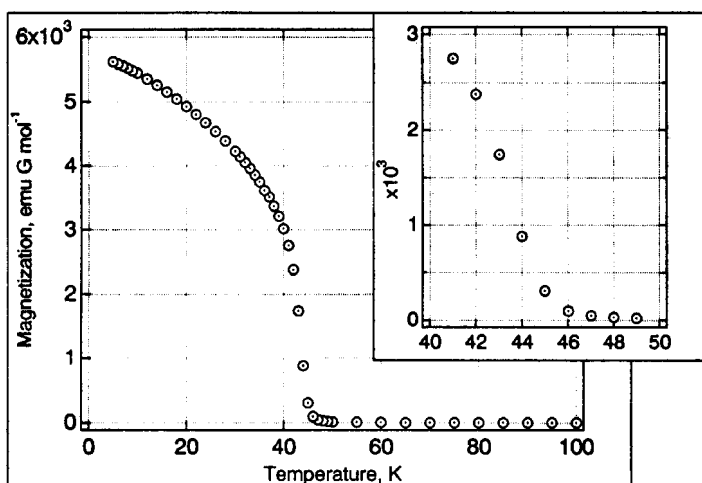


Fig. 7 Observed temperature dependencies of magnetization for [Mn(II)(hfac) $_2$] $_3$ ·9 $_2$ at a field of 5 Oe.

CONCLUSION

Assemblage and ordering of the unpaired electrons of high-spin polynitroxide radicals in macroscopic scale have been effectively achieved by means of coordination with paramagnetic 3d transition metal ions. These heterospin systems promise the versatile design principle for high T_C molecule-based magnets (15). It has been made clear that there are two major factors contributing to high T_C in such materials: higher dimensionality of the magnetic structure of the complexes, and strong exchange coupling within the polynitroxide ligand molecules and through the coordination bonds. Thus the design and construction of polyradical ligands capable of producing well-defined 3-D structures remain to be explored systematically as discussed by Kahn *et al.* (17) and suggested to be instrumental in developing T_C above 300 K in V(TCNE) $_2$ · π CH $_2$ Cl $_2$ (18). Exploitation of the inherent advantages of molecular systems and endowing molecule-based magnetic materials with additional molecular properties, e. g., photochemical and NLO properties, is suggested to be a viable direction for developing useful molecule-based magnetic materials (19).

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REFERENCES

1. H.Iwamura. *Pure Appl.Chem.* **58**, 187 (1986). Y.Teki *et al. J.Am.Chem.Soc.* **105**, 3722 (1983); **108**, 2147 (1986). T.Sugawara *et al. J.Am.Chem.Soc.* **106**, 6449 (1984); **108**, 368 (1986).
2. I.Fujita *et al. J.Am.Chem.Soc.* **112**, 4074 (1990).
3. K.Itoh. *Chem.Phys.Lett.* **1**, 235 (1967). E.Wasserman *et al. J.Am.Chem.Soc.* **89**, 5076 (1967). N.Mataga. *Theor.Chem.Acta* **10**, 372 (1968).
4. N.N.Tyutyulkov *et al. Int.J.Quantum Chem.* **29**, 1325 (1986). K.Matsuda *et al. J.Am.Chem.Soc.* **117**, 5550 (1995).
5. N.Nakamura *et al. J.Am.Chem.Soc.* **114**, 1484 (1992). N.Nakamura *et al. Angew.Chem.,Int.Ed.Engl.* **32**, 872 (1993).
6. A.Caneschi *et al. Progr.Inorg.Chem.* **39**, 331 (1991). A.Caneschi *et al. D.Gatteschi et al. eds. Magnetic Molecular Materials*, NATO ARI Series E, Kluwer Academic Publishers, p. 215 (1991). C.Benelli *et al. Inorg.Chem.* **28**, 3089 (1989).
7. (a) A.Calder *et al. J.Am.Chem.Soc.* **91**, 3724 (1969). (b) K.Mukai *et al. Bull.Chem.Soc.Jpn.* **48**, 2381 (1975). (c) T.Ishida and H.Iwamura, *J.Am.Chem.Soc.* **113**, 4238 (1991). (d) F.Kanno *et al. J.Phys.Chem.* **97**, 13267 (1993).
8. T.Mitsumori *et al. J.Am.Chem.Soc.* **117**, 2467 (1995).
9. K.Inoue and H.Iwamura. *J.Am.Chem.Soc.* **116**, 3173 (1994).
10. R.Uchiyama and H.Iwamura, unpublished results.
11. K.Inoue and H.Iwamura. *J.Chem.Soc., Chem. Commun.* **1994**, 2273.
12. H.M.McConnell. *J.Chem.Phys.* **39**, 1910 (1963). A.Izuoka *et al. J.Am.Chem.Soc.* **109**, 2631 (1987).
13. K.Inoue *et al.* Submitted for publication in *J. Am. Chem. Soc.*
14. K.Inoue and H.Iwamura, *Adv.Mater.* in press.
15. (a) J.S.Miller *et al. Chem.Rev.* **88**, 201 (1988). (b) J.S.Miller and D.A.Dougherty, eds., *Ferromagnetic and High Spin Molecular Based Materials*, *Mol.Cryst.Liq.Cryst.* **176** (1989). (c) D. Gatteschi *et al. eds. Magnetic Molecular Materials*, NATO ARI Series E, Kluwer Academic Publishers, E198 (1991). (d) H.Iwamura and J.S.Miller, eds. *Chemistry and Physics of Molecular Based Magnetic Materials*, *Mol.Cryst.Liq.Cryst.* **232** and **233** (1993). (e) J.S.Miller and A.J. Epstein. *Angew.Chem., Int.Ed.Engl.* **33**, 385 (1994). (f) A.Rajca. *Chem.Rev.* **94**, 871 (1994).
16. M.Hitzfeld *et al. Phys.Rev. B*, **29**, 5023, (1984). O.Kahn, *Organic and Inorganic Low-Dimensional Crystalline Materials*; P.Delhaes, M.Drillon, eds., NATO ASI Series 168; Plenum; New York, 1987; p. 93.
17. H.O.Stumpf *et al. J. Am. Chem. Soc.* **115**, 6738 (1993). H.O.Stumpf *et al. Science* **261**, 447 (1993).
18. J.M.Manriquez *et al. Science* **252**, 1415 (1991).
19. N.Koga and H.Iwamura, to be published elsewhere.