Exchange Coupling Parameters and Energy Levels for Cyclic Metal-Radical Complexes of Bis(hexafluoroacetylacetonato)manganese(II) with 5-*tert*-Butyl-1,3-phenylenebis(*N*-*tert*-butylaminoxyl) and (4-*N*-*tert*-Butyl-*N*-oxyamino)pyridine

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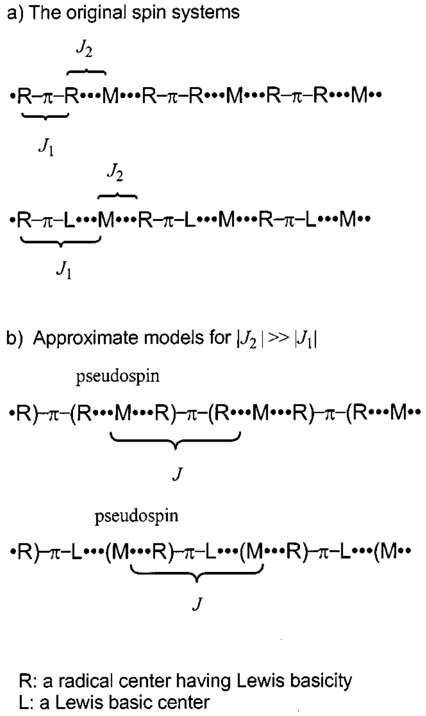
Keywords: Manganese / Radicals / Cyclic dimer complexes / Exchange coupling parameters / Spin states

Temperature-dependent paramagnetic susceptibility data for two cyclic dimer complexes of bis(hexafluoroacetylacetonato)manganese(II) with 5-*tert*-butyl-1,3-phenylenebis(*N*-*tert*-butylaminoxyl) and 4-(*N*-*tert*-butyl-*N*-oxyamino)pyridine have been analyzed to obtain two sets of two intramolecular exchange coupling parameters J_1 and J_2. A previous model, based on one of these interactions being much weaker than the other, could not be explicitly correlated to these actual exchange-coupling parameters. However, the energy levels of the low-lying spin states were found to be reproduced reasonably well by the approximate method.

Introduction

Coordination polymers $(R-\pi-R-M)_n$ and $(R-\pi-L-M)_n$, consisting of magnetic metal ions M and basic free radicals R−π−R and R−π−L with two ligating sites, constitute recent highlights in molecular-based magnets since they afford samples exhibiting high Curie temperatures in the range 3.4−46 K.[1] It is very often the case that there are two or more kinds of exchange pathways in such systems (Scheme 1) and, therefore, the temperature dependence of the paramagnetic susceptibility data is not simple to analyze rigorously.[2] As a first approximation, such spin systems may be analyzed by assuming a model in which one of the interactions is much stronger than the other. Then high-temperature susceptibility data would be regarded as governed by the stronger interaction, and lower temperature data would be approximated by the development of the weaker interactions between the pseudo-spins already established at the high temperature.[3−6] The physical meaning of the effective exchange coupling thus obtained is not understood straightforwardly. We have attempted to make the physical meaning of such effective exchange coupling clearer by taking advantage of the cyclic units in which the numbers of the spins are finite and rigorous solutions of the spin Hamiltonian are feasible.



Scheme 1. Schematic presentation of the spin systems

Results and Discussion

Cyclic Coordination Complex of Bis(hexafluoroacetylacetonato)manganese(II) with {5-*tert*-Butyl-1,3-phenylenebis(*N*-*tert*-butylaminoxyl)} (1)

The 1:1 complex $[Mn(hfac)_2\mathbf{1}]_2$ was obtained by reaction of bis(hexafluoroacetylacetonato)manganese(II) $[Mn(hfac)_2]$

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with the diradical 5-*tert*-butyl-1,3-phenylenebis(*N*-*tert*-butylaminoxyl) (**1**).[3] Its crystal structure (Figure 1) shows that it is a cyclic analog of previously described 1-D complex polymers made up of similar components without ring *tert*-butyl groups or with halogen substituents in their place.[1b,1e] The molecule consists of two Mn^{II} ions ($S = 5/2$) and four aminoxyl radicals ($S = 1/2$) arranged in a ring as shown in Scheme 2.

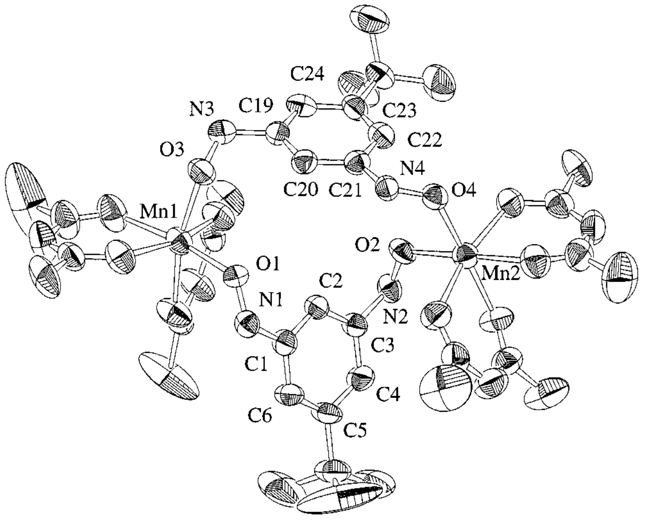
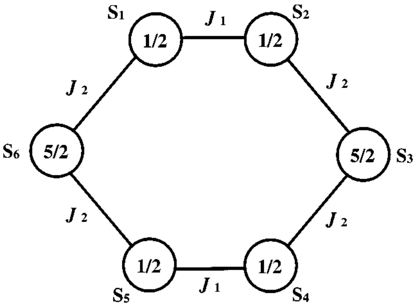
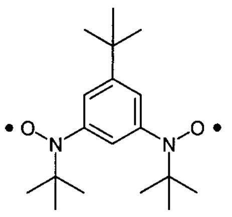


Figure 1. Structure of the cyclic complex $[Mn(hfac)_2\mathbf{1}]_2$; fluorine atoms, *N*-*tert*-butyl groups and hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level



Scheme 2. A cyclic arrangement of the spins in $[Mn(hfac)_2\cdot\mathbf{1}]_2$



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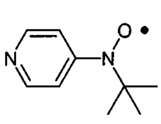

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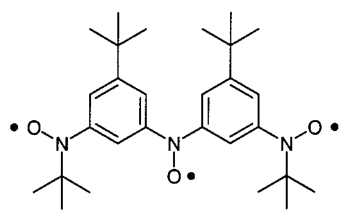


3

The molar paramagnetic susceptibility χ of the complex was investigated in the temperature range 2−300 K. The χT values exhibit a continuous increase from room temperature down to ca 50 K, reaching a plateau at 5.71 Kcm^3mol^{-1} (Figure 2). This value agrees well with the theoretical spin-only value for a $S = 3$ spin ground state, which can be explained from a ferromagnetic (F) interaction between two $S = 3/2$ pseudo-spins [5/2 − (2 × 1/2)], obtained by assuming a predominant antiferromagnetic (AF) coupling (J_2) between the manganese(II) ions and the two coordinated radicals. This high-spin ground state is stabilized with respect to the upper energy levels by a few hundred wavenumbers, as deduced from the decrease of χT upon increasing temperature. A decrease of χT at the lowest temperatures may be analyzed in terms of intermolecular AF coupling.

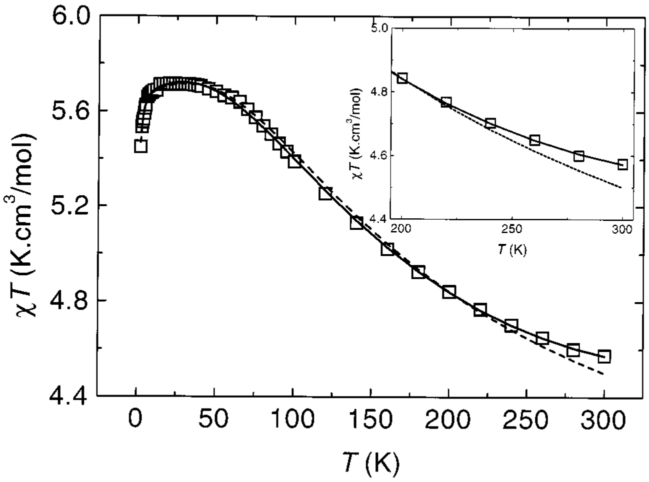


Figure 2. Dependence of the χT product on temperature T for the $[Mn(hfac)_2\mathbf{1}]_2$ complex; full and broken curves correspond to the best-fit theoretical curves based on the exact and approximate solutions, respectively (see text); the high-temperature region is expanded and shown in Inset

On this basis, the experimental data were fitted in a previous paper[7] by using a model of dimers of $S = 3/2$ pseudo-spins, with the exchange constant J and a molecular field contribution to account for the weak inter-dimer interactions. Note that the high temperature value of 4.57 Kcm^3mol^{-1} is significantly higher than that expected for two isolated $S = 3/2$ spins, suggesting a strong ferromagnetic coupling. The best agreement between theory and experiment was found for $J = +68.6$ K (±0.6 K), a Weiss constant of $\theta = -0.10$ K, and a Lande factor g = 2.002, taking into account a scaling factor of 0.954 related to sample quality, errors in sample weighing, etc.[3] However, above 220 K, the calculated data are somewhat lower than the experimental data points (see broken curve in Figure 2). Similar analysis of a chain polymer consisting of bis(hexafluoroacetylacetonato)manganese(II) and *m*-phenylenebis(*N*-*tert*-butylaminoxyl) in a 1:1 ratio gives a ferromagnetic exchange constant $J = +23$ K (±5 K) for repeating $S = 3/2$ units.[4] In these analyses, J is an "effective" interaction between pseudo-spins, and it is assumed that the Mn−aminoxyl AF interaction J_2 is much more efficient than the F intraligand aminoxyl−aminoxyl one (J_1).

Clearly, such a description may be improved by considering the rigorous spin Hamiltonian of the magnetic system:

$$\mathbf{H} = -J_1(S_1S_2 + S_4S_5) - J_2(S_2S_3 + S_3S_4 + S_5S_6 + S_6S_1) - g\mu_B H\sum S_i \tag{1}$$

corresponding to the sum of the exchange (H_{ex}) and field dependent contributions. In this expression, J_1 and J_2 are the exchange constants defined above, $S_i = 5/2$ for $i = 3$, (6 manganese(II) ions) and $S_i = 1/2$ for the others (aminoxyl radicals). The g factor is assumed to be 2.0 for both spin carriers (isotropic spins).

The energy levels of H_{ex} were determined by using as basis functions $|F_i>$ the direct products of the individual spin states $|m_{si}>$ quantified through their z component. Owing to the values of the m_{si} components, the total number of basis functions is $6^2 \times 2^4 = 576$. Taking into account the spin space symmetry, the size of the largest block to be diagonalized is reduced to 84 × 84.

The energy levels of the magnetic system are given by the eigenvalues of the exchange matrix whose coefficients are given by the products $<F_i|H_{ex}|F_j>$. They are obtained numerically by diagonalization of the matrix $[H_{ij}]$ (see Experimental Section); the temperature dependence of the magnetic susceptibility χ is then deduced from the usual expression:[8]

$$\chi = \frac{Ng^2\mu_B^2\sum M_{S_i}^2 \exp(-E_i / kT)}{kT\sum(2S_i + 1)\exp(-E_i / kT)} \tag{2}$$

For comparison with the experimental data, this expression has been modified by taking the molecular field contribution into account with the Curie-Weiss law. The best result, illustrated in Figure 2 for the parameters $J_1 = +1005$ K (±11 K), $J_2 = -539$ K (±19 K), and Weiss constant $\theta = -0.10$ K (±0.01 K), with a scaling factor 0.954,[9] gives a very good description of the experimental data over the whole temperature range. Simulation of the high-temperature values was very much improved: from 4.50 to 4.57 $\mathrm{Kcm^3mol^{-1}}$ for the observed value of 4.58 $\mathrm{Kcm^3mol^{-1}}$ at 300 K (see solid curve in Figure 2). It thus appears that the pseudo-spin approximation is not valid to determine the actual interactions. Indeed, unlike the assumption made previously, the radical-radical interaction (J_1) is found to be stronger than the manganese(II)−radical one (J_2). Furthermore, the value of J_1 is about 30 times greater than that refined in the pseudo-spin approximation. Let us recall that the "efficiency" of the exchange interaction depends also on the spin values; the energy is actually governed by ≈ JS^2. As a result, the aminoxyl−aminoxyl and Mn−aminoxyl interaction energies are shown to be 1005 × (1/2)(1/2) = 251 K and −539 × (5/2)(1/2) = −674 K, respectively. The latter remains stronger but does not justify the neglect of J_1 with respect to J_2. This result is in agreement with the fact that the room temperature value of χT is significantly higher than that expected for two independent $S = 3/2$ pseudo-spins.

Using the refined values of J_1 and J_2, the energy levels obtained for the above system are plotted in Figure 3 for the different spin S. It appears that the low lying levels correspond to S ranging from 3 to 0, according to the energy scheme expected for a ferromagnetic dimeric unit of $S = 3/2$ spins. These energy levels are contrasted in Figure 4 with those of the $S = 3/2$ dimer exhibiting an exchange constant $J = +68.6$ K, as reported above. A clear similarity between the two diagrams explains why the dimer approximation gives quite a satisfactory fit to the experimental data. Indeed, the energy gap between the $S = 3$ and $S = 2$ levels in the dimer model is shown to be $3J = +205.8$ K which is similar to that obtained for the real system, $\Delta E = f(J_1, J_2) \approx 190$ K.

Within the present model, all the energy levels of the hexamer system are taken into account for the calculation of $\chi T = f(T)$, while only 4 levels are involved in the dimer approximation. Thus, as the higher energy levels are neglected, the experimental susceptibility is not well reproduced at high temperature (dashed curve in Figure 2).

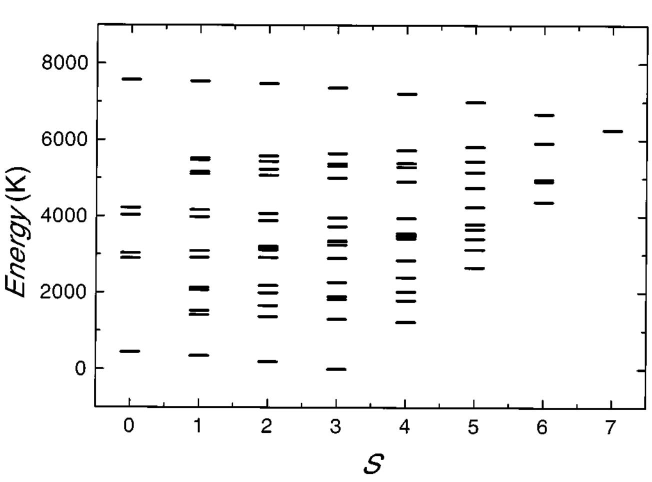


Figure 3. An energy level diagram calculated for the magnetic hexamer with the refined values of J_1 and J_2

Cyclic Coordination Complex of Bis(hexafluoroacetylacetonato)manganese(II) with 4-(*N*-*tert*-Butyl-*N*-oxyamino)pyridine (2)

The complex $[\mathrm{Mn(hfac)_2}\mathbf{2}]_2$ was obtained by reaction of bis(hexafluoroacetylacetonato)manganese(II) with the radical 4-(*N*-*tert*-butyl-*N*-oxyamino)pyridine **(2)** in a 1:1 ratio.[5] The crystal structure (Figure 5) shows that it consists of two $\mathrm{Mn^{II}}$ ions ($S = 5/2$) and two aminoxyl radicals ($S =$

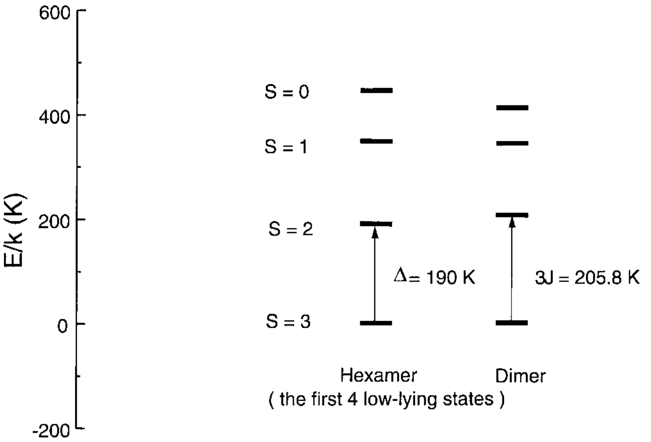


Figure 4. Comparison between the low-lying energy levels as obtained from the hexamer model and the dimer approximation for $[Mn(hfac)_2\mathbf{1}]_2$

1/2) forming a four-spin ring as illustrated in Scheme 3. The manganese atoms are coordinated to the pyridyl nitrogen atom on one side and the aminoxyl radical ligand, through the oxygen, on the other. Thus, two different exchange constants J_1 and J_2 have to be considered.

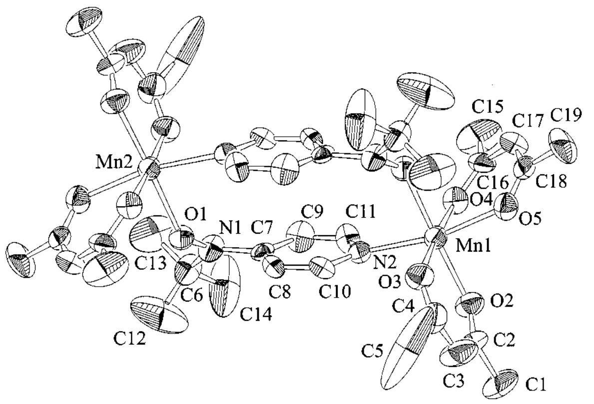
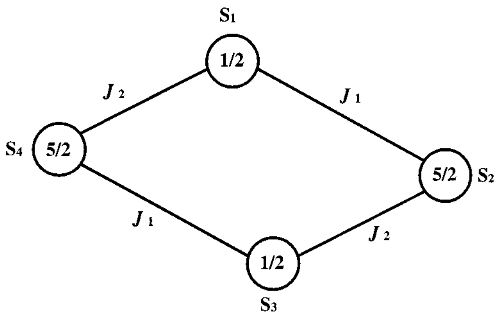


Figure 5. ORTEP view of the cyclic complex $[Mn(hfac)_2\mathbf{2}]_2$ at 30% probability; hydrogen atoms are omitted for clarity



Scheme 3. A cyclic arrangement of the spins in $[Mn(hfac)_2\cdot\mathbf{2}]_2$

The magnetic susceptibility has been investigated in the range 2.5−300 K (Figure 6). The χT versus T plot shows a continuous increase from 6.4 Kcm^3mol^{-1} at 300 K to 9.97 Kcm^3mol^{-1} at 2.5 K. The high temperature value is close to that expected for two noninteracting $S = 2$ spins, whereas the low temperature behavior agrees with that of an $S = 4$ ground state ($g = 2$). In reference to the previous Mn^{II}−radical complex, the magnetic behavior of this system may be described as ferromagnetic dimers of $S = 2$ pseudo-spins, arising from strong AF interactions between the directly bonded manganese(II) and aminoxyl centers. The experimental data, tentatively fitted to the dimer model by assuming two $S = 2$ pseudo-spins, are well reproduced for the effective interaction $J = +8.70$ K and $g = 1.97$ (see broken curve in Figure 6).

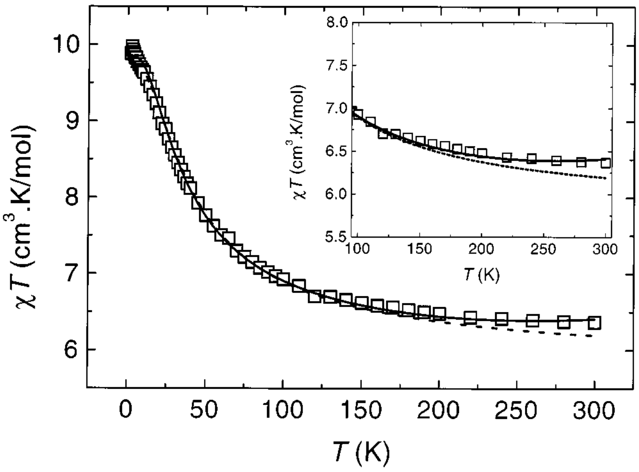


Figure 6. Variation of the χT vs T for the $[Mn(hfac)_2\mathbf{2}]_2$ complex; full and broken curves correspond to the best-fit theoretical curves based on the exact and approximate solutions, respectively (see text); the high-temperature region is expanded and shown in Inset

In the same way as above, and in order to compare the Mn−NO interactions in both systems, the actual spin Hamiltonian for the cyclic array of four spins, expressed as:

$$\mathbf{H} = -J_1(S_1S_2 + S_3S_4) - J_2(S_2S_3 + S_4S_1) - g\mu_B H\Sigma S_i \qquad (3)$$

has been solved exactly. In this expression, J_1 and J_2 now stand for the exchange pathways between the Mn^{II} and NO through the pyridine ring and the direct coordination bond, respectively (Scheme 3). This model gives a very good agreement between theoretical and experimental susceptibility data, especially in the high temperature region (Figure 6), for the refined parameters $J_1 = -22.6$ K (±0.1 K), $J_2 = -372$ K (±9 K) and a scaling factor of 0.980. All the exchange couplings are antiferromagnetic, and a ferrimagnetic ground-state is stabilized. Note that the former value is in good agreement with the exchange constant of −24.8 K[9] between Mn^{II} and aminoxyl radical through the 4-pyridyl unit in the mononuclear 1:2 complex [Mn(hfac)2**2**2].[5] In this complex, the Mn^{II} ion is only coordinated to the pyridyl nitrogen atoms.

The energy scheme, corresponding to the refined values of J_1 and J_2, is contrasted to that for the $S = 2$ dimer in Figure 7. The energy gap between the ground state and the first excited state is shown to be $4J = +34.8$ K in the dimer limit, in very good agreement with that obtained for the exact model based on Equation 3 (34.8 K).

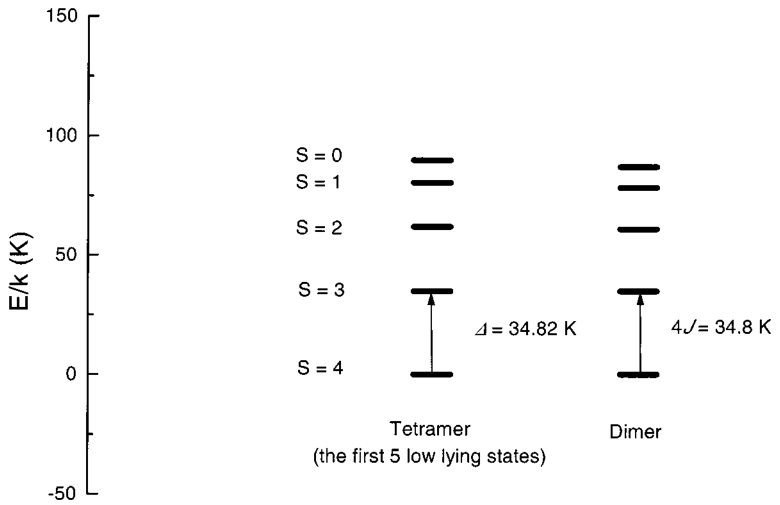


Figure 7. Comparison between the low-lying energy levels as obtained by using the tetramer model and the dimer approximation for $[Mn(hfac)_2\mathbf{2}]_2$

The Exchange Coupling Parameters J_1 and J_2 Obtained by Exact Solution

These are summarized in Table 1. The intraligand NO−NO interaction (J_1) obtained for $[Mn(hfac)_2\mathbf{1}]_2$ is as large as 10^3 K. From a classical-classical and quantum-classical chain model, Markosyan and co-workers obtained $J_1 \geq 350$ K for a 3-D complex of $[Mn(hfac)_2]$ with the tris(-aminoxyl) triradical **3** which has a *m*-phenylene connectivity.[4] The χT values for the free ligand **1** stay constant at 1 Kcm^3mol^{-1} between 4 K and room temperature, confirming that the corresponding J_1 value should be much larger than 300 K.[10] The intraligand NO−NO coupling in the neat triradical **3** is 480 K.[10][11] The value obtained in this study serves as the first example in which the magnitude of the ferromagnetic coupling parameter in *m*-phenylenebis(aminoxyl) compounds has been determined rigorously. The ferromagnetic J_1 values in these compounds originate from the in-phase spin polarization of the π-electrons on the *m*-phenylene rings due to their topology. The limited data available seem to suggest that the magnitude of such F coupling increases upon complexation with magnetic metal ions. Accumulation of more data is necessary before such a conclusion is confirmed.

It should be noted that all the direct Mn^{II}−NO exchange interactions through coordination bonds represented by J_2 are of the same order: −539, −372, and −520 K for $[Mn(hfac)_2\mathbf{1}]_2$, $[Mn(hfac)_2\mathbf{2}]_2$, and $[\{Mn(hfac)_2\}_3\mathbf{3}_2]$ $_2$, respectively. Gatteschi et al. obtained similar AF coupling values ranging from −210 to −430 K for the coupling of Mn^{II} with 2-substituted 4,4,5,5-tetramethyl-4,5-dihydro-3-oxylimidazol-1-oxides, so called Ullman′s nitronyl nitroxides. The AF interactions derive from the pairing of the unpaired electrons in the dπ metal and pπ ligand orbitals.

Finally, we note that the indirect Mn^{II}−NO exchange coupling through the 4-pyridyl unit is AF: −22.6 and −24.8 K for cyclic $[Mn(hfac)_2\mathbf{2}]_2$ and mononuclear 1:2 complex $[Mn(hfac)_2\mathbf{2}_2]$, respectively.[5][10] The π-electrons on the pyridine ring should be polarized in such a way that the 3- and 5-carbons and the ring nitrogen atom carry positive spin which in turn overlap with the π-type d-orbital of the magnetic Mn^{II} ion attached to the pyridyl nitrogen atom. The reduced AF interaction is reasonable considering the Mn^{II} complex of bis(4-pyridyl)carbene.[13]

Table 1. Comparison of the related exchange coupling parameters

Radical or metal-radical complex	J_1/K intraligand NO - NO	J_1/K Mn(II) - NO via the 4-pyridyl unit	J_2/K directly coordinated Mn(II) - NO
$[Mn(hfac)_2{\bullet}\mathbf{1}]_2$	1005 ± 11		-539 ± 19
1	>300		
$[\{Mn(hfac)_2\}_3{\bullet}\mathbf{3}_2]$	>350		-520
3	480 ± 40		
$[Mn(hfac)_2{\bullet}\mathbf{2}]_2$		-22.6 ± 0.1	-372 ± 9
$[Mn(hfac)_2{\bullet}\mathbf{2}_2]$		-24.8 ± 0.2	
$[Mn(acac)_2{\bullet}\mathbf{2}_2]$		-20.4 ± 0.1	

Conclusion

Is there a merit in the pseudo-spin model for analyzing the temperature-dependence of the magnetic susceptibility of complex magnetic systems? Note that, whereas the energy values of the spin states are directly proportional to J in the dimer units, they are nonlinear combinations of J_1 and J_2 in the polymeric complexes investigated. As a result, J is an "effective" interaction with no physical meaning, and cannot be related to the actual interactions (even the sign may differ) in the latter, except when one interaction is negligible. Finally, let us point out that the use of such pseudo-spin models has an important merit of giving an insight into the splitting of the low lying spin-states. The information obtained here should be useful,[14][15] for the comparison of the exchange interactions in extended heterospin systems and for the design of such new systems.

Experimental Section

Preparation of the Complexes: The cyclic dimer complexes [Mn(hfac)$_2$**1**]$_2$[3] and [Mn(hfac)$_2$**2**]$_2$[5] were prepared by mixing bis(hexafluoroacetylacetonato)manganese(II) with radical ligands **1** and **2** in a 1:1 ratio as described previously.

X-ray Structures: The structures and magnetic data for cyclic complexes [Mn(hfac)$_2$**1**]$_2$[3] and [Mn(hfac)$_2$**2**]$_2$[5] have already been reported. Crystallographic data (excluding structure factors) for the structures [Mo(hfac)$_2$**1**]$_2$ and [Mo(hfac)$_2$**2**]$_2$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-114418 and -135189, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, GB-Cambridge CB2 1EZ, UK [Fax: int. code + 44/1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]..

Magnetic Measurements: Fine crystalline samples were mounted in a capsule (Japan Pharmacopoeia No. 5, o. d. 4.5 × 11 mm) and measured on a Quantum Design MPMS-5S SQUID susceptometer at 500 G. Corrections for the diamagnetic contribution of the samples were made by using Pascal's constants. The diamagnetic contribution of sample capsules and holding straws used was in the range -3.7×10^{-5} − -6.7×10^{-5} emu.G.

Theoretical/Computational Analysis of the Magnetic Susceptibility Data: *SPIN*, a computer program for calculation and analysis of the magnetic properties of low dimensional systems, was employed.[16] An optimized diagonalization vectorial subroutine was used, from the library of the French institute for development and means in computer science, IDRIS (Orsay, France); the MINUIT function minimization program of the CERN library (CERN, Geneva, Switzerland) was used as a minimization subroutine.

Acknowledgments

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[7] Strictly speaking it is J/k_B rather than J itself which is given in the unit of K; 1 K corresponds to 0.695 cm^{-1}.

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[9] Scaling factors employed here contains all the errors due to the sample purity, weighing the samples, calibration of SQUID susceptometer, etc. in addition to the deviation of the g factor from 2.00 as assumed in this study. If the last term is predominant, $f = g2$ and, therefore, $f = 0.954$ corresponds to a g factor of 1.95 ($= 2 \times \sqrt{0.954}$).

[10] Since spin Hamiltonian $H = -2J(S_1S_M + S_MS_2)$ is used in ref.[5][10] the actual exchange constant is $2J$.

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