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Synthesis, Structure, and Magnetic Properties of a Cyclic Dimer of Bis(hexafluoroacetylacetonato)-{1,3-bis(*N*-*tert*-butyl-*N*-oxylamino)-5-*tert*-butylbenzene}manganese(II)

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Coordination polymers exhibiting T_c values in the range 3.4−46 K have been obtained by the reaction of bis(hexafluoroacetylacetonato)manganese(II) [=Mn(hfac)$_2$] with *m*-phenylene-linked bis and tris nitroxide radicals as polydentate ligands.[1]

However, the magnetic coupling in such compounds is not easy to understand and remains only partially solved on a theoretical level so far.[2] Cyclic oligomers which have only a small number of coupling spins may permit the determination of the different intermolecular exchange coupling constants which can then be used for the theoretical description of the magnetic properties of analogous polymer materials. Therefore the study of the magnetic properties of small cyclic compounds can provide insight into the spin coupling mechanism in compounds where a diradical is linked to manganese(II) ions as in the case of cyclic oligomers as well as of coordination polymers. In this note, we report the synthesis, crystal structure, and magnetic properties of the cyclic dimer complex **1**, consisting of a dinitroxide diradical and Mn(hfac)$_2$ units, in analogy to the known polymer systems.[1]

Dimer **1** was synthesized by a standard procedure.[1] A suspension of 101 mg (0.2 mmol) of Mn(hfac)$_2$·2H$_2$O in 100 mL of *n*-heptane was refluxed to remove the water of hydration azeotropically. The resulting solution (50 mL) was cooled to room temperature, and 1 mL of diethyl ether was added to dissolve the precipitated Mn(hfac)$_2$. To this solution was added 61 mg (0.2 mmol) of the diradical 1,3-bis(*N*-*tert*-butyl-*N*-oxylamino)-5-*tert*-butylbenzene **2**[3] in 40 mL of dichloromethane/diethyl ether (5:2), and the dichloromethane and ether were evaporated under reduced pressure. After 1 h, 125 mg (0.08 mmol, 80%) of **1** was isolated as black microcrystals. Single crystals were obtained by slow evaporation. Anal. Calcd for $C_{28}H_{32}F_{12}N_2O_6Mn$: C, 43.37; H, 4.16; N, 3.61. Found: C, 43.32; H, 4.20; N, 3.61.

The X-ray crystal structure analysis of **1** reveals that it consists of an alternating cyclic array of two Mn(hfac)$_2$ units and two diradical units (Figure 1, Table 1). The manganese(II) ions have a distorted octahedral coordination environment, and all Mn−O bond lengths and Mn−O−N bond angles compare closely to those found in the 1-D chain coordination polymer **3**[1] (Table 2). In analogy to polymer **3**,[1b] the two manganese(II) ions of one dimer molecule have either a ΔΔ or a ΛΛ configuration.

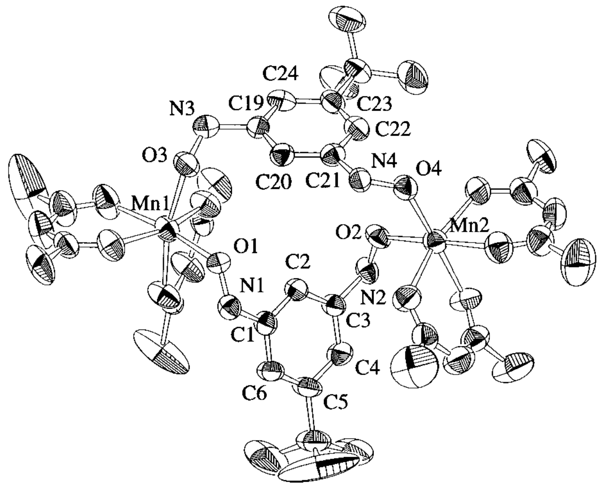

Figure 1. Structure of the cyclic dimer **1**. The CF$_3$ moieties, the *tert*-butyl groups of the nitroxide moieties, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The enantiomer containing the Λ configuration at the two metallic centers is shown.

In contrast to the case of **3**, where within one polymer chain all diradicals have the same configuration, the configurations of the two diradical ligands in **1** are different. However, according to theoretical considerations,[4] the configuration of the *tert*-butyl nitroxide groups should have only a minor influence on the exchange coupling in **2** in the range of torsion angles for **1** and for polymer **3**. Thus spin interactions in the cyclic dimer **1** should be comparable to those in polymer **3**.

The monoclinic unit cell of **1** contains four dimer molecules which are related by symmetry operations so that only one independent molecule exists in the crystal lattice. Each molecule is well shielded by trifluoromethyl and *tert*-butyl groups, and no specific strong intermolecular contact could be found which alone could be of importance for the discussion of intermolecular spin interactions.

The EPR spectrum of a solid sample of **1** at room temperature showed three broad unstructured lines. The peak-to-peak width of the central line was 550 G at $g = 2.00$. The temperature dependence of the molar susceptibility of a microcrystalline sample of **1** was measured on a SQUID susceptometer at 500 G in the temperature range 2−300 K (Figure 2).

The $\chi_M T$ value of 4.576 emu K mol^{-1} at 300 K corresponds favorably to those found for the analogous polymers **3**. Assuming a strong antiferromagnetic interaction between the spins of the manganese(II) ions and the spins of the directly bound organic radical ligand, the high-temperature $\chi_M T$ value of 4.576 emu K mol^{-1} per dimer unit can be assigned to two uncoupled effective spins of $S = {}^3/_2$, even if the experimental value is somewhat higher than the theoretically expected value

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(1) (a) Iwamura, H.; Inoue, K.; Hayamizu, T. *Pure Appl. Chem.* **1996**, *68*, 243. (b) Iwamura, H.; Inoue, K.; Koga, N. *New J. Chem.*, in press.

(2) (a) Coronado, E.; Drillon, M.; Georges, R. In *Research Frontiers in Magneto Chemistry*; O'Connor, C. J., Ed.; World Scientific: Singapore, 1993; Chapter 2. (b) Preliminary results of a theoretical study of polymers **3** gave values of about 70 Kk_B for the exchange coupling via the *m*-phenylene linker. This result is not compatible with the exchange coupling greater than 300 Kk_B found for the free diradicals: Private communication from M. Drillon and P. Rabu of IPCMS, France.

(3) (a) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1993**, *97*, 13267. (b) Kanno, F. Master Thesis, University of Tokyo, 1992.

(4) Fang, S.; Lee, M. S.; Horvart, D. A.; Borden, T. W. *J. Am. Chem. Soc.* **1995**, *117*, 6727.

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Table 1. Crystallographic Data for **1**

empirical formula $[C_{28}H_{32}F_{12}N_2O_6Mn]_2$	space group $P2_1/c$ (No. 14)
fw 1550.98	$T = 23 \pm 1$ °C
$a = 15.631(10)$ Å	$\lambda = 0.710\ 69$ Å
$b = 11.271(9)$ Å	$\rho_{calcd} = 1.452$ g cm^{-3}
$c = 40.29(1)$ Å	$\mu = 4.75$ cm^{-1}
$\beta = 91.63(4)°$	$R(F_o)^a = 0.074$
$V = 7096(5)$ Å^3	$R_w(F_o)^a = 0.052$
$Z = 4$	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Selected Bond Parameters for **1**[a]

Bond Lengths/Å			
Mn(1)−O(1)	2.101(6)	O(3)−N(3)	1.314(10)
Mn(1)−O(3)	2.102(6)	O(4)−N(4)	1.308(10)
Mn(2)−O(2)	2.069(6)	N(1)−C(1)	1.41(1)
Mn(2)−O(4)	2.084(6)	N(2)−C(3)	1.44(1)
O(1)−N(1)	1.286(9)	N(3)−C(19)	1.45(1)
O(2)−N(2)	1.298(9)	N(4)−C(21)	1.36(1)
Bond Angles/deg			
O(1)−Mn(1)−O(3)	87.0(2)	Mn(2)−O(4)−N(4)	129.4(5)
O(2)−Mn(2)−O(4)	89.3(2)	O(1)−N(1)−C(1)	117.7(7)
Mn(1)−O(1)−N(1)	128.1(5)	O(2)−N(2)−C(3)	114.5(7)
Mn(1)−O(3)−N(3)	126.2(5)	O(3)−N(3)−C(19)	115.0(7)
Mn(2)−O(2)−N(2)	122.1(5)	O(4)−N(4)−C(21)	118.0(7)
Torsion Angles/deg			
O(1)−N(1)−C(1)−C(2/6)	18		
O(2)−N(2)−C(3)−C(2/4)	39		
O(3)−N(3)−C(19)−C(20/24)	24		
O(4)−N(4)−C(21)−C(20/22)	16		

[a] Selected bond parameters for the analogous coordination polymer **3**[1] are as follows. Distances/Å: Mn−O• 2.097(3), 2.079(3); O−N 1.302(5), 1.296(5); N−C(Ar) 1.419(6), 1.424(6). Angles/deg: •O−Mn−O• 86.7(1); Mn−O−N 126.0(3), 124.3(2); O−N−C(Ar) 115.8(4), 115.6(4). Torsion angles/deg: •O−N−C(Ar)−C(*o*-Ar) 30, 46. d_{MnMn}: in **1**, 7.488(4) Å; in **3**, 8.560(1) Å. Some very short C−C bond lengths were found in one of the aromatic rings of **1**: $d_{C(19)C(20)} = 1.36(1)$ Å, $d_{C(22)C(23)} = 1.35(1)$ Å.

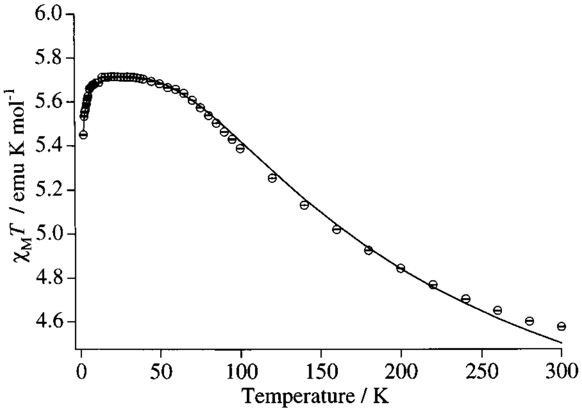

Figure 2. $\chi_M T$ vs T plot for dimer **1** at 500 G. The solid line is the best fit curve according to eq 1 (for parameters see text).

of 3.759 emu K mol^{-1}. A model in which the ferromagnetic coupling between the two nitroxide radical molecules is stronger in magnitude than the antiferromagnetic coupling between the Mn(II) and the directly bound radical should have given a high-temperature value of 10.776 emu K mol^{-1}.

Upon a reduction in the temperature, the $\chi_M T$ value of **1** increases and reaches a plateau at 38 K. The average of $\chi_M T$ in the range of the plateau from 38 to 14 K is 5.714 emu K mol^{-1} and can be assigned to a spin of $^6/_2$ in a first approximation (theoretically 6.014 emu K mol^{-1}). Below 14 K, $\chi_M T$ rapidly decreases with decreasing temperature, indicating an intermolecular antiferromagnetic interaction.

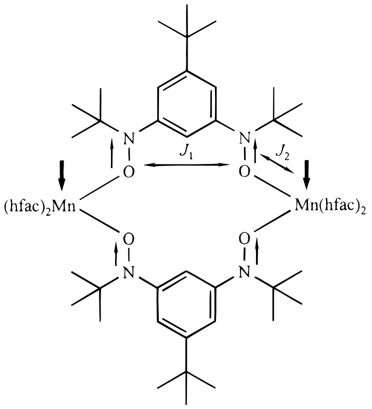

Figure 3. Coupling pattern in the cyclic dimer **1**.

The quantitative interpretation of the magnetic susceptibility data should be carried out according to the HDvV formalism for an cyclic array of six spins of $^1/_2$, $^1/_2$, $^5/_2$, $^1/_2$, $^1/_2$, $^5/_2$, defined by the two kinds of exchange parameters shown in Figure 3. Neglecting the zero-field splitting and assuming $|J_2| \gg |J_1|$, from the spin Hamiltonian $\mathbf{H} = -2J(\mathbf{S_1}\cdot\mathbf{S_2})$, eq 1 was derived,[5] where all symbols have their usual meaning. Intermolecular antiferromagnetic interactions were taken into account by the introduction of the Weiss constant Θ. A constant value of 2.002 for the Landé factor g was used, and a correction factor f which adjusts for the purity and weighing errors of the sample, other experimental errors, and approximations of the model used was introduced.

$$\chi_M T = \frac{2Nfg^2\beta^2 T}{k(T-\Theta)}\ \frac{e^{J/k_BT} + 5e^{3J/k_BT} + 14e^{6J/k_BT}}{1 + 3e^{J/k_BT} + 5e^{3J/k_BT} + 7e^{6J/k_BT}} \qquad (1)$$

Least-squares fitting of the $\chi_M T$ data with eq 1 leads to $J = 68.6 \pm 0.6$ K $= 47.7 \pm 0.4$ cm^{-1}, $\Theta = -0.099 \pm 0.005$ K, and $f = 0.954 \pm 0.001$. Equation 1 describes the experimental $\chi_M T - T$ curve quite well at temperatures lower than 220 K. At high temperatures, the experimental $\chi_M T$ values are somewhat higher than those obtained from eq 1. This could possibly be explained by the population of spin states other than $S = {}^6/_2$ and $S = {}^3/_2$ and indicates that J_2 cannot be neglected in reference to k_BT at 300 K.

Dimer **1** provides a compound which is a cyclic analogue of previously described coordination polymers of similar composition. The temperature dependence of the magnetic susceptibility of **1** can be interpreted in the framework of the HDvV formalism by the coupling of two spin centers with $S = {}^3/_2$ which exhibit ferromagnetic coupling to give an $S = {}^6/_2$ ground state. The deviation of the so calculated curve from the experimental values could be caused by the population of further spin states. The average value of $J = 68.6$ K found for the coupling of two spins of $S = {}^3/_2$ in the cyclic dimer **1** could fit favorably to the coupling constant of 70 Kk_B obtained in a theoretical study for polymer **3**.[2b] However, the different topologies of **1** and **3** cannot be neglected and make a more detailed study necessary for a sound discussion of the coupling mechanisms in **1** and **3**. The theoretical treatment of a hexagonal spin system with spins of $^5/_2$, $^1/_2$, $^1/_2$, $^5/_2$, $^1/_2$, $^1/_2$ could provide further information about these spin states and yield the coupling constant for the *m*-bis(*N*-*tert*-butyl-*N*-oxylamino)benzene unit. A detailed theoretical analysis of such a six-spin system is in progress.[6,7]

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(5) Kahn, O. *Molecular Magnetism*; VCH Publishers: Weinheim, Germany, 1993; p 114.

(6) In collaboration with M. Drillon and P. Rabu of IPCMS, France.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of complex **1** is available on the Internet only. Access information is given on any current masthead page.

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(7) A parallel study of **1** has been performed by K. Inoue of the Institute of Molecular Science, Okazaki, Japan.