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Structure and magnetic properties of a ring of four spins formed by manganese(II) and a pyridine substituted nitronyl nitroxide

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Abstract

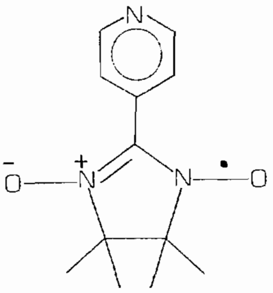
A compound of formula [Mn(hfac)$_2$NITpPy]$_2$, where hfac = hexafluoroacetylacetonato and NITpPy = (2-(4-pyridyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), was synthesized. The X-ray analysis showed that it crystallizes in the monoclinic $P2_1/n$ group with $a = 10.995(2)$, $b = 15.378(2)$, $c = 17.990(3)$ Å, $\beta = 106.58(1)°$, and $Z = 2$. The manganese ions are octahedrally coordinated by the four oxygen atoms of the hfac ligands, an oxygen of a nitronyl nitroxide radical, and the pyridine nitrogen of another radical, related by the inversion center to the first one, thus yielding a dinuclear structure. The uncoordinated NO groups are at short distances from the ones translated along the a axis. The magnetic data suggested that in the four spins system the antiferromagnetic interaction between manganese and radical through the NO group dominates and that a weak ferromagnetic interaction through the pyridine might be responsible for the diamagnetic ground state. The analysis however is not unambiguous due to the presence of short contacts between radicals.

Introduction

The last few years have seen a dramatic increase in the number of reports of different spin clusters [1–3]. In particular many novel magnetic behaviors have been observed when clusters containing different types of spins have been reported [4–7].

Nitronyl nitroxides, NITR, which are paramagnetic ligands have largely contributed to the extension of the observed magnetic behaviors yielding for instance ferrimagnetic rings, ferrimagnetic chains, clusters of twelve spin, and stabilizing unusual ground spin states [8–11].

In an attempt to synthesize molecular based ferromagnets using metal ions and radicals as building blocks [12], we considered pyridine substituted NITR radicals in order to have additional donor atoms to bind to the metal ions and in perspective to assemble an extended structure with magnetic dimensionality larger than one. The final aim would be that of increasing the critical temperature of these novel materials.



NITpPy

We have reported complexes containing the radical (2-(4-pyridyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), NITpPy, in which the metal ion is bound only to the pyridine nitrogen of the radical and we have observed a weak coupling between the paramagnetic metal ion and the radical is present [13, 14]. In particular we found that with copper(II) and nickel(II) the coupling is antiferromagnetic while with manganese(II) it is weakly ferromagnetic.

We have now obtained a complex of formula [Mn(hfac)$_2$NITpPy]$_2$, where hfac = hexafluoroacetylacetonato, in which both the pyridine and a NO group of the radical are coordinted to metal ions and we report here its structure and magnetic properties.

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Experimental

Synthesis of the complex

$Mn(hfac)_2 \cdot 2H_2O$ and NITpPy were prepared as previously described [15, 16]. An amount of 0.25 mmol of $Mn(hfac)_2 \cdot 2H_2O$ was dissolved in hot n-heptane then 0.25 mmol of NITpPy were added. Immediately a green microcrystalline precipitate appeared. It was identified by elemental analysis as a 1:1 stoichiometric adduct. The solution containing the precipitate was stored for ten days at 8 °C and all the green precipitate changed into dark green–blue well shaped crystals. They were collected and analyzed well for $Mn(hfac)_2$NITpPy. *Anal.* Calc. for $C_{22}F_{12}H_{18}MnN_3O_6$: C, 37.55; H, 2.56; N, 5.97. Found: C, 37.62; H, 2.59; N, 5.86%.

Magnetic measurements

Variable temperature magnetic susceptibility was measured by using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF1200S continuous-flow cryostat and a Bruker B-E15 electromagnetic operating at 1.35 T. Diamagnetic corrections were estimated from Pascal's constants.

X-ray data collection

X-ray data for $[Mn(hfac)_2NITpPy]_2$ were collected on a Nicolet four circle diffractometer equipped with Mo Kα radiation and a graphite monochromator. Accurate unit cell parameters were derived from least-squares refinement of the setting angles of 20 machine-centered reflections and are reported with other experimental parameters in Table 1. The data were corrected for Lorentz and polarization effects but not for absorption. The $P2_1/n$ space group was unambiguously determined by the extinctions. The Patterson map revealed the position of the manganese atom, while the positions of the other non-hydrogen atoms were found by successive Fourier and difference Fourier synthesis using the SHELX76 package [17]. All non-hydrogen atoms were defined with anisotropic thermal factors, and the final least-squares refinement, including the contribution of the hydrogen atoms in idealized positions, converged to $R = 7.37$. The highest peak in the last difference

TABLE 1

Crystallographic data and experimental parameters for $[Mn(hfac)_2NITpPy]_2$

Formula	$C_{22}F_{12}H_{18}MnN_3O_6$
Formula weight	703.32
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.995(2)
b (Å)	15.378(2)
c (Å)	17.990(3)
β (°)	106.58(1)
Density (g cm^{-3})	1.602
V (Å^3)	2915.3
μ (cm^{-1})	5.47
Z	4
Temperature (°C)	22
λ (Å)	0.7107
$R(F_o)$	0.0737
$R_w(F_o)$	0.0898

TABLE 2

Atomic coordinates and isotropic thermal factors for $[Mn(hfac)_2NITpPy]_2$

	x/a	y/b	z/c	B_{eq}
Mn	0.0190(1)	0.2121(1)	0.0961(1)	3.65(2)
O1	−0.1711(4)	0.2076(3)	0.0230(2)	3.81(13)
O2	−0.4309(6)	0.0097(4)	0.0956(4)	6.61(19)
O3	−0.0267(4)	0.1203(3)	0.1771(3)	4.68(15)
O4	0.2024(4)	0.2141(3)	0.1866(3)	5.12(16)
O5	0.0895(4)	0.3067(3)	0.0336(3)	4.57(15)
O6	−0.0182(5)	0.3219(3)	0.1585(3)	5.43(16)
N1	−0.2648(4)	0.1746(3)	0.0444(3)	3.22(13)
N2	−0.3823(5)	0.0814(3)	0.0830(3)	4.23(17)
N3	−0.0998(5)	−0.1098(3)	−0.0359(3)	3.40(15)
N3′	0.0998(5)	0.1098(3)	0.0359(3)	3.40(13)
C1	−0.2840(6)	0.0900(4)	0.0527(3)	3.31(17)
C2	−0.3751(7)	0.2282(4)	0.0527(4)	4.58(22)
C3	−0.4241(7)	0.1684(5)	0.1047(4)	4.60(22)
C4	−0.2195(6)	0.0206(4)	0.0250(3)	3.30(17)
C5	−0.1948(6)	0.0306(4)	−0.0453(4)	3.79(18)
C6	−0.1365(6)	−0.0352(4)	−0.0735(4)	3.79(19)
C7	−0.1256(6)	−0.1187(4)	0.0322(4)	3.87(19)
C8	−0.1834(6)	−0.0568(4)	0.0647(4)	3.95(19)
C9	−0.4695(9)	0.2290(6)	−0.0316(5)	7.54(32)
C10	−0.3351(8)	0.3169(5)	0.0799(6)	6.97(34)
C11	−0.5658(7)	0.1685(5)	0.0939(5)	5.87(28)
C12	−0.3531(9)	0.1829(6)	0.1906(5)	6.58(29)
C13	0.0326(7)	0.1092(5)	0.2475(4)	4.90(21)
C14	0.2200(6)	0.1933(5)	0.2559(4)	4.95(22)
C15	0.1461(7)	0.1406(6)	0.2884(5)	5.68(27)
C16	−0.0362(10)	0.0461(7)	0.2865(5)	9.05(40)
C17	0.3432(9)	0.2321(7)	0.3091(5)	7.81(31)
C18	0.1266(7)	0.3816(4)	0.0556(4)	4.58(23)
C19	0.0371(7)	0.3936(5)	0.1634(5)	5.19(24)
C20	0.1056(8)	0.4269(5)	0.1179(5)	5.82(26)
C21	0.2047(9)	0.4254(5)	0.0096(5)	6.71(33)
C22	0.0195(11)	0.4477(6)	0.2331(6)	7.70(32)
F1	−0.1470(6)	0.0242(5)	0.2514(4)	12.07(29)
F2	0.0172(10)	−0.0289(7)	0.2945(9)	21.51(64)
F3	−0.0295(13)	0.0650(7)	0.3538(4)	22.37(64)
F4	0.3281(7)	0.3086(6)	0.3264(6)	17.63(41)
F5	0.4369(5)	0.2243(6)	0.2856(4)	15.04(34)
F6	0.3759(7)	0.1941(8)	0.3799(4)	15.60(41)
F7	0.2143(7)	0.5090(4)	0.0178(4)	11.85(38)
F8	0.3187(6)	0.3954(4)	0.0273(5)	12.30(30)
F9	0.1557(8)	0.4131(6)	−0.0640(4)	13.84(30)
F10	0.0550(8)	0.4045(5)	0.2968(4)	13.00(32)
F11	0.0890(10)	0.5160(5)	0.2462(5)	16.54(48)
F12	−0.0943(7)	0.4706(5)	0.2225(4)	13.20(30)

Fourier map was less than 0.4 e/Å^3. Atomic positional parameters are listed in Table 2; see also 'Supplementary material'.

Result and discussion

Crystal structure

The crystal structure of [Mn(hfac)$_2$NITpPy]$_2$ consists of centrosymmetric dimers, as shown in Fig. 1. Each manganese(II) ion is hexacoordinated by four oxygen atoms belonging to the hfac fragments, one oxygen atom of the NITpPy radical and the nitrogen atom of the pyridine ring belonging to the symmetry related molecule. Selected bond lengths and angles are reported in Table 3. The coordination octahedron is distorted and the bond distances range from 2.17–2.27 Å, the longest being the Mn–N bond. The N–O distance of the uncoordinated oxygen of the radical is shorter than that of the coordinated one, 1.27 versus 1.30 Å, as generally observed [8, 9, 18]. The carbon atoms of the five membered ring of the radical carrying the methyl groups are not in the plane of unsaturation, being 0.2 Å below and above the average plane. The dihedral angle of this plane with that of the pyridine ring is 38.9°. The two pyridine rings of the dimeric unit can be considered as stacked; the distance between the planes is 3.37 Å, and the shortest contact between two atoms belonging to different rings, C6–N3′, is 3.56 Å. The uncoordinated oxygen of the radical, O2, is at 3.35 Å from the centrosymmetric one of a molecular unit translated along the *a* axis. From the magnetic point of view this short contact generates chains of dimers which develop along the *a* crystallographic axis. The average planes of the interacting radicals are parallel to each other, being related by the inversion center, and they form an angle of 79° with the plane defined by the two NO groups, O2N2O2′N2′. The other geometric parameter which plays an important role in the magnetic interaction is the angle O2–N2–O2′ which is 70°.

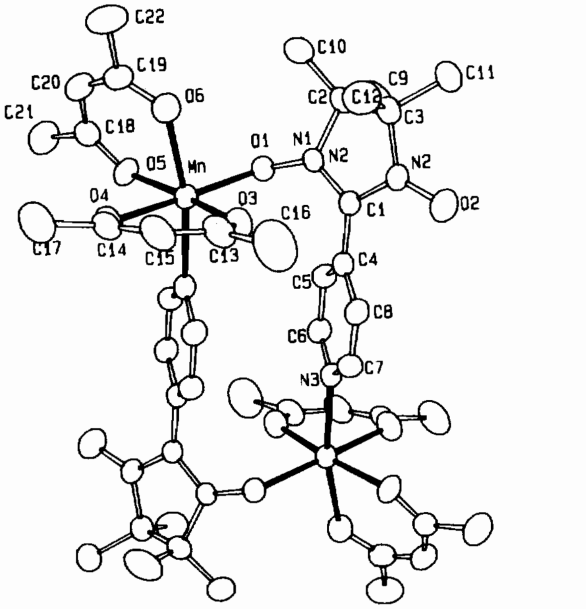


Fig. 1. ORTEP view at 50% probability of the molecular structure of [Mn(hfac)$_2$NITpPy]$_2$. Only the asymmetric unit is labelled.

TABLE 3

Selected angles (°) and bond distances (Å) for [Mn(hfac)$_2$NITpPy]$_2$[a]

O6–Mn–N3′	167.5(2)	O5–Mn–N3′	88.2(2)
O5–Mn–O6	83.7(2)	O4–Mn–N3′	87.8(2)
O4–Mn–O6	82.7(2)	O4–Mn–O5	89.2(2)
O3–Mn–N3′	93.9(2)	O3–Mn–O6	92.6(2)
O3–Mn–O4	81.5(2)	O1–Mn–N3′	97.6(2)
O1–Mn–O6	92.9(2)	O1–Mn–O5	97.9(2)
O1–Mn–O3	91.1(2)		
Mn–O1	2.129(4)	Mn–O3	2.188(5)
Mn–O4	2.201(4)	Mn–O5	2.118(5)
Mn–O6	2.130(6)	Mn–N3′	2.234(5)
O1–N1	1.301(7)	O2–N2	1.274(8)
N1–C1	1.334(7)	N2–C1	1.348(9)

[a] Standard deviations in the last significant digit are in parentheses.

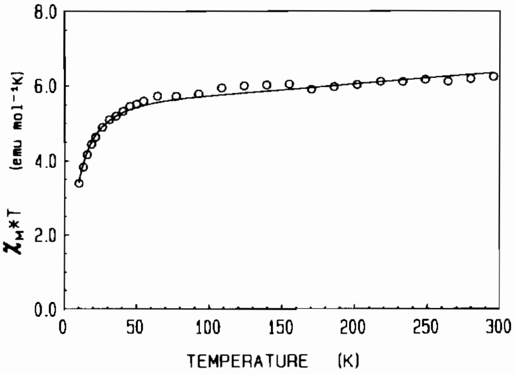


Fig. 2. Temperature dependence of the magnetic susceptibility in the form χT vs. T. The solid line represents the fitting obtained with $J_{R\text{-}M} = 146$ cm^{-1}, $J'_{R\text{-}M} = -2.7$ cm^{-1}, and $J_{M\text{-}M} = 0.5$ cm^{-1} (see text).

Magnetic properties

The temperature dependence of the magnetic susceptibility is shown in Fig. 2. The room temperature value of χT for a dimeric unit is 6.23 emu K mol^{-1} ($\mu_{eff} = 7.06$), much lower than the value expected for two $S = 5/2$ and two $S = 1/2$ uncorrelated spins ($\mu_{eff} = 8.72$) but very close to that expected for two weakly coupled $S = 2$ spins ($\mu_{eff} = 6.92$). On lowering the temperature the χT product decreases steadily and a faster decrease is observed below 60 K. At 10 K the χT value is 3.38 emu K mol^{-1} ($\mu_{eff}=5.2$).

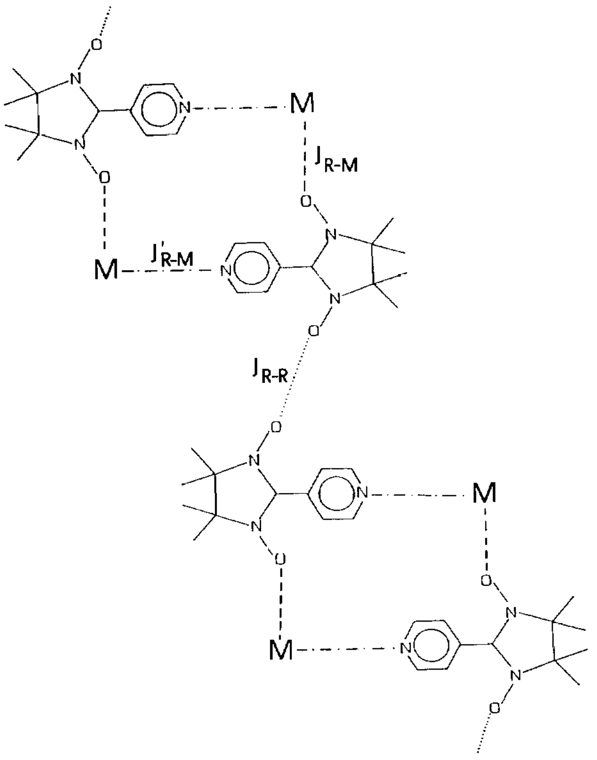
The analysis of the magnetic properties of this system is rather complicated due to the presence of different pathways of magnetic interaction. Since the radical bridges two manganese ions in a non-symmetrical fashion, two J values are necessary to describe the magnetic behavior of this system: J_{R-M} refers to the coupling of the radical with the oxygen bonded manganese ion while J'_{R-M} describes the interaction with the nitrogen bonded manganese. The short contacts between NO groups of radicals belonging to different molecular units suggest the presence of a non-negligible interaction described by a coupling constant J_{R-R} as shown in Scheme 1. In addition, since the bridging radical provides an exchange pathway between the two metal ions, a J_{M-M} parameter must be included in the model.

In order to analyze the data it is necessary to make some preliminary checks about the relative importance of these J constants. First of all the relatively low value of the magnetic moment at room temperature indicates that a strong antiferromagnetic interaction must be operative. Comparison with a large number of data concerning manganese(II) ions bound to nitroxides through the oxygen of the NO group suggests that the antiferromagnetic interaction through the NO group dominates [8]. This means that we can expect that in the pairs formed by the manganese ion and the radical which is bound to it through the oxygen atom the spins are essentially coupled in a ground $S=2$ state even at room temperature. This agrees with the value of μ_{eff} in the range 60–300 K which in fact suggests the presence of two weakly coupled $S=2$ states.

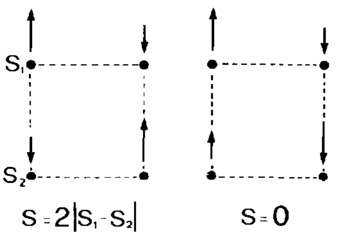
Previous studies on mononuclear compounds in which the radical is bound to manganese(II) only through the pyridine have revealed the presence of weak ferromagnetic interaction of about 1 cm^{-1} [14]. The results have been justified in terms of orbital pathways involving the π^* molecular orbital, the pyridine nitrogen lone pair, and the magnetic orbital of the metal. In particular admixing of the nitrogen lone pair in the π^* magnetic orbital of the radical is expected in the present case where the angle between the pyridine plane and the ONCNO plane of the radical is largely different from 0°.

Rings of four different spins like those observed in the structure of [Mn(hfac)$_2$NITpPy]$_2$ are already known. When only antiferromagnetic coupling is present between different spins the ground states are $2|S_1-S_2|$, as shown in Scheme 2, and these can be considered as the simplest ferromagnetic rings. In fact the compound of formula [Mn(F$_3$bzac)$_2$NITMe]$_2$, previously reported, was found to have a ground $S=4$ state [19]. However if ferro- and antiferromagnetic interactions alternate, as we are suggesting in the present case, the ground spin state becomes non-magnetic. So the counter-intuitive result of changing the sign of two coupling constants from antiferro- to ferromagnetic is that of going from a high spin to a diamagnetic ground state.

Neglecting any inter-dimer interaction the magnetic susceptibility has been reproduced with a model which also takes into account the coupling between manganese ions. The best fit values are $J_{R-M}=146$ cm^{-1}, $J_{R-M}=-2.7$ cm^{-1}, and $J_{M-M}=0.5$ cm^{-1} with



Scheme 1.



Scheme 2.

$r = 3.01 \times 10^{-4}$*, the spin Hamiltonian being defined as $H = JS_1 \cdot S_2$.

Direct interaction between nitronyl nitroxide radicals through uncoordinated oxygens at a relatively short distance one from the other has already been observed [9, 13, 18], and coupling constants ranging from 7.4 to 135 cm^{-1} depending on the geometrical parameters have been obtained by numerical fittings. The inter-dimer interaction in the present case cannot be neglected and complicates the pattern of magnetic interactions generating a chain of dimers. Because no models are available to calculate the magnetic susceptibility of such a system we simply notice here that an antiferromagnetic interaction $J_{\text{R-R}}$ may also justify the decrease in χT at low temperature. If, in order to make the system tractable, we neglect the weak intra-dimer interactions, $J'_{\text{R-M}}$, we fall again in the case of four coupled spins. With $J_{\text{R-M}} = 145$ cm^{-1} and $J_{\text{R-R}} = 64$ cm^{-1} we reproduced satisfactorily the observed magnetic susceptibility with the agreement factor $r = 7.62 \times 10^{-4}$ which is a little higher than the previous one. The high value obtained for $J_{\text{R-R}}$ through the uncoordinated NO groups seems in agreement with previous findings [13].

Therefore although a satisfactory analysis of the magnetic properties of $[\text{Mn(hfac)}_2\text{NITpPy}]_2$ could not be achieved due to the inherent complication of the system the model with a strong antiferromagnetic $J_{\text{R-M}}$ coupling constant was confirmed. The observed decrease in χT at low temperature may be due to a weak ferromagnetic $J'_{\text{R-M}}$ and/or to a moderate antiferromagnetic $J_{\text{R-R}}$.

The most interesting result of this investigation is that NITpPy ligands can bind to metal ions through both the pyridine nitrogen and the NO groups. Although in this case a dimeric structure connected by an NO–NO interaction resulted, it seems possible to obtain an extended structure which can be formed if all the three donor atoms of the radicals are bound to metal ions. we are currently attempting to isolate these extended systems.

Supplementary material

Detailed reports for structure determination including experimental parameters, anisotropic thermal factors, coordinates of hydrogen atoms, interatomic distances, intramolecular angles, and structure factors (22 pages) are available from the authors on request.

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*r is defined as $(\Sigma(\chi T_{\text{obs}} - \chi T_{\text{calc}})^2/\Sigma(\chi T_{\text{obs}})^2)^{1/2}$.