5510 *Inorg. Chem.* **2000,** *39,* 5510−5514

Novel Square Planar Copper(II) Complexes with Imino or Nitronyl Nitroxide Radicals Exhibiting Large Ferro- and Antiferromagnetic Interactions

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Received May 23, 2000

This paper reports the synthesis, crystal structures, and magnetic properties of two copper(II) complexes (**1, 2**) of general formula $Cu(tfac)_2(radical)_2$ (tfac = trifluoroacetate; radical = (**1**) 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITPh) or (**2**) 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazoline-1-oxyl (IMPh)). They crystallize in the monoclinic $P2_1/n$ space group with the following parameters: (**1**) $a = 13.212(2)$ Å, $b = 9.136(1)$ Å, $c = 15.587(2)$ Å, $\beta = 114.61(1)°$, $Z = 2$; (**2**) $a = 11.059(2)$ Å, $b = 15.289(1)$ Å, $c = 10.694(2)$ Å, $\beta = 114.20(1)°$, $Z = 2$. In both complexes the copper(II) ion is coordinated to two radicals in a slightly distorted square planar surrounding. The copper(II)−radical exchange couplings are antiferromagnetic for the nitronyl nitroxide (NITPh) complex (**1**) and ferromagnetic in the case of the imino nitroxide (IMPh) analogue (**2**). The ground state has been found to be a spin-doublet for **1** and the spin-quartet for **2**. No thermal population of the highest states has been observed, indicating copper(II)−radical couplings of $|J| > 500$ cm^{-1}.

Introduction

The past decade has triggered fast-growing interest in nitroxide free radicals, as building blocks in the engineering of molecular based magnet. The reasons are mainly that they are among the most stable open shell organic molecules, even in combination with metal ions, where they can also act as bridging ligands. This has allowed a large extent of chemical modifications that have led to the efficient and specific formation of a remarkable variety of magnetic species, which may be either wholly organic compounds[1−5] or based on metal−radical complexes.[6−10]

Our contribution to this field focuses mainly on the metal−radical approach[11,12] with the aim of synthesizing compounds exhibiting spontaneous magnetization. Accordingly, we work at the synthesis of nitronyl nitroxide free radicals designed to afford extended polynuclear complexes, with strong metal−radical magnetic interactions. In this frame we have recently reported on lamellar compounds based on a 2D network of alternatively bound nitronyl nitroxide radicals and manganese(II) ions which behave as a magnet below 50 K.[9]

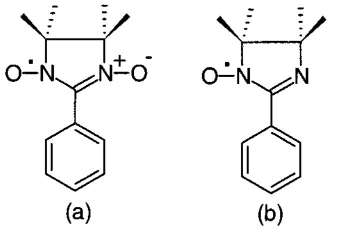

Figure 1. Chemical structure of (a) nitronyl nitroxide (NITPh) and (b) imino nitroxide (IMPh).

Herein, we report on the structure and magnetic properties of two novel copper(II)−radical complexes: one has been obtained with the nitronyl nitroxide radical NITPh; the second one, with the imino nitroxide IMPh analogue (Figure 1). Both compounds exhibit opposite but large metal−radical magnetic interactions: antiferromagnetic for the nitronyl nitroxide complex; ferromagnetic in the case of the imino nitroxide analogue. For both compounds, the nature of the magnetic interaction is understood in relation with the copper(II)−radical coordination geometry.

Experimental Section

Syntheses. 2,3-Bis(hydroxylamino)-2,3-dimethylbutane, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NITPh), and 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazoline-1-oxyl (IMPh) were prepared according to literature methodes.[13,14] Other compounds were used as purchased.

$Cu(tfac)_2(NITPh)_2$ (1). Bis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)bis(trifluoroacetato)copper(II) was prepared by adding

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10.1021/ic0005590 CCC: $19.00

Table 1. Summary of the Crystal Structure Data Collection and Refinement for 1 and **2**

	1	**2**
formula	$CuC_{30}H_{34}N_4O_8F_6$	$CuC_{30}H_{34}N_4O_6F_6$
fw	756.2	724.2
T (K)	298(2)	298(2)
space group	$P2_1/n$	$P2_1/n$
a (Å)	13.212(2)	11.059(2)
b (Å)	9.136(1)	15.289(1)
c (Å)	15.587(2)	10.694(2)
β (deg)	114.61(1)	114.20(1)
V (Å^3)	1710.5(4)	1649.3(4)
Z	2	2
m(Mo Kα) (mm^{-1})	0.724	0.743
d_{calc} (cm^3)	1.468	1.458
λ (Å)	0.71060	0.71060
R(I),[a] $I > 2\sigma(I)$	0.0394	0.0583
$R_w(F^2)$,[a] $I > 2\sigma(I)$	0.1085	0.1280

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w(F^2) = \Sigma[wF_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

145 mg of copper trifluoroacetate hydrate in 10 mL of diethyl ether in which was dissolved 233 mg of NITPh. To the resulting green-brown solution was added 10 mL of heptane. Concentration and cooling to −18 °C yielded air-stable parallelepipedic dark green crystals. (250 mg, 66%). Anal. Calcd for $C_{30}H_{34}N_4O_8F_6Cu$: C, 47.65; H, 4.53; N, 7.41; O, 16.93; F, 15.07; Cu, 8.40. Found: C, 47.49; H, 4.68; N, 7.44; F, 14.27; Cu, 8.20

Cu(tfac)$_2$(IMPh)$_2$ (2). Bis(2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazoline-1-oxyl)bis(trifluoroacetate)copper(II) was also prepared as air-stable parallelepipedic dark-brown crystals (220 mg, 60%) in a similar manner using 145 mg of copper trifluoroacetate hydrate and 218 mg of IMPh in a mixture of ethyl ether and heptane. Anal. Calcd for $C_{30}H_{34}N_4O_6F_6Cu$: C, 49.76; H, 4.73; N, 7.74; O, 13.26; F, 15.75; Cu, 8.78. Found: C, 49.39; H, 4.79; N, 7.60; F, 15.36; Cu, 8.71

X-ray Crystallography. The intensity data were collected in the $\omega-2\theta$ mode, at room temperature, on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator for the Mo Kα (λ = 0.7106 Å) radiation. Cell constants were derived from the least-squares fit of the setting angles for 25 selected reflections with $10° \leq \theta \leq 15°$. The structures were solved and refined using the SHELXTL[15] software. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated position with isotropic thermal parameters. Crystal structure and refinement data for compounds **1** and **2** are summarized in Table 1.

Magnetic Susceptibility Measurements. The magnetic susceptibilities were measured on the bulk materials in the 2−300 K temperature range with a Quantum Design MPMS superconducting SQUID magnetometer operating at a field strength of 0.5 T. The data were corrected for diamagnetism of the constituent atoms using Pascal constants.

Results and Discussion

Description of the Structures. Views of the molecular structures of **1** and **2** are shown respectively in Figure 2 and Figure 3. Selected bond lengths (Å) and angles (deg) are listed in Table 2.

Cu(tfac)$_2$(NITPh)$_2$ (**1**). The molecular unit of **1** consists of one (trifluoroacetate)copper(II) moiety (Cu(tfac)$_2$) bound with two radicals (NITPh) through an oxygen atom of one of their NO groups (Figure 1). The molecule is centrosymmetrical with the copper(II) ion at the inversion center. The Cu−O3(carboxylate) distance is 2.992(4) Å, so that the trifluoroacetate (tfac) anion is unidentate with the copper(II) ion in a slightly distorted square planar surrounding. The distances Cu−O1(carboxylate) and Cu−O4(nitroxyl) are 1.895(4) and 1.956(4) Å, respectively, and the O1−Cu−O4 angle is 92.5(2)°. The N1−O4 bond length is 1.308(5) Å and departs markedly from those observed for the uncoordinated N2−O2 in **1** and **2,** respectively, 1.267(6) and 1.263(5) Å (Table 2). The lengthening of the N−O bond is a general trend observed in the coordination of nitronyl nitroxide radicals, and the N1−O4 bond length is in agreement with previous reports.[16] Generally the more marked is the lengthening the stronger is the magnetic interaction. The torsion angle between the nitronyl nitroxide fragment and the phenyl ring is 24.84°. The geometrical features relevant for the understanding of the magnetic properties are given hereafter. The angle Cu−O4−N1 is 121.7(3)°. The O4−N1−C3−N2−O2 plane containing the unpaired electron makes angles of 86.98 and 86.72° respectively with the Cu−O4−N1 and the O1−Cu−O4 planes. The shortest intermolecular distances between the uncoordinated NO groups are greater than 4 Å (O2−O2ii, 4.095(8) Å; O2−N2ii, 4.938(7) Å (ii: 1 − x, −y, −z)).

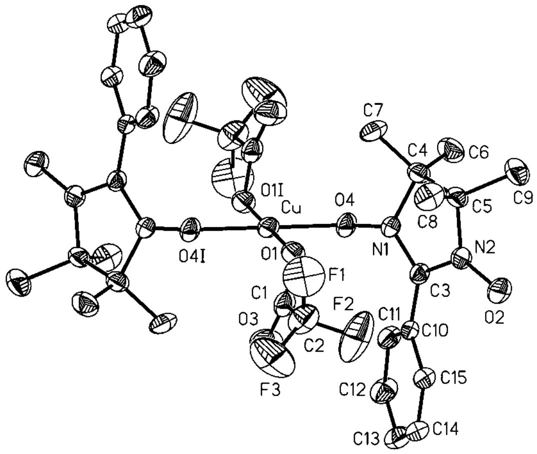

Figure 2. View of Cu(tfac)$_2$(NITPh)$_2$ (**1**) with ellipsoids drawn at the 30% probability level.

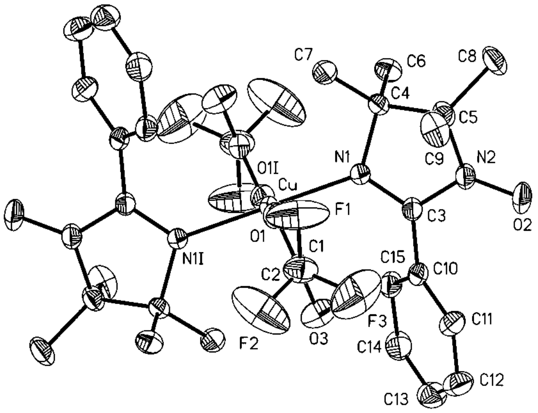

Figure 3. View of Cu(tfac)$_2$(IMPh)$_2$ (**1**) with ellipsoids drawn at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1	**2**
Cu−O1	1.895(4)	1.948(4)
Cu−O4	1.956(4)	
Cu−O3	2.992(4)	3.012(5)
Cu−N1		1.995(2)
O2−N2	1.267(6)	1.263(5)
O4−N1	1.308(5)	
O1−Cu−O4	92.5(2)	
O1−Cu−N1		88.7

Cu(tfac)$_2$(IMPh)$_2$ (2). The molecular structure of **2** is similar to that of **1,** but with the imino nitroxide (IMPh) in place of the

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[15] *SHELXTL,* Ver. 5.030; Bruker AXS: 1994.

[16] Caneschi, A.; Gatteschi, D.; Rey, P. *Prog Inorg. Chem.* **1991**, *30*, 331.

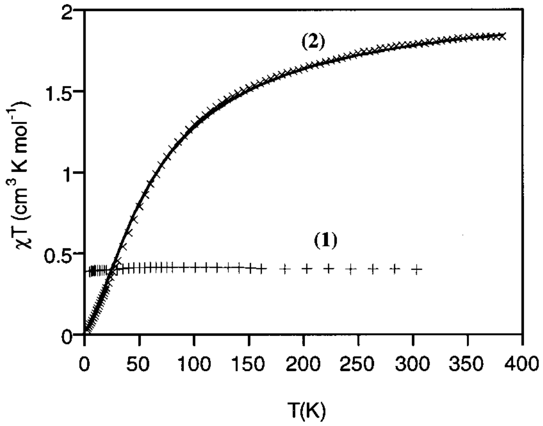


Figure 4. Thermal dependence of the χT product for Cu(tfac)$_2$(NITPh)$_2$ (**1**) and Cu(tfac)$_2$(IMPh)$_2$ (**2**). The solid line for **2** is calculated with the parameters reported in the text.

nitronyl nitroxide (Figure 2). As for **1**, the molecular unit of **2** consists of one (trifluoroacetate)copper(II) (Cu(tfac)$_2$) bound with two radicals (IMPh). The radicals are coordinated to the copper(II) ion through the imino nitrogen atom, due to its strong donor character. Here again the trifluoroacetate (tfac) is unidentate, and the molecule, centrosymmetrical at the copper(II) ion in a square planar surrounding. The distances Cu−O1-(carboxylate) and Cu−N1(imino) are respectively 1.948(4) and 1.995(4) Å, and the O1−Cu−N1 angle is 88.7(2)°. The torsion angle between the imino nitroxide fragment and the phenyl ring is 37.80°. The geometrical features relevant for the magnetic properties are as follows: the copper plane O1−Cu−N1 makes angles of 83.18 and 89.6° with the N1−C3−N2−O2 and Cu−N1−C3 planes, respectively. The shortest intermolecular distances found between the uncoordinated NO groups for compound **2** (O2−O2ii, 3.390(9) Å; O2−N2ii, 3.473(7) Å (ii: 1 − *x*, −*y*, −*z*)) are noticeably shorter than those for **1**.

Magnetic Properties. The temperature dependence of the magnetic susceptibility χ has been measured down to 2 K for both complexes **1** and **2**. The results are displayed in the form of the product of the magnetic susceptibility with the temperature (χT) versus the temperature (T) in Figure 4 for both compounds **1** and **2**.

Cu(tfac)$_2$(NIT2Ph)2 (1). $\chi T = 0.4$ emu K mol^{-1} at room temperature and obeys a Curie law when the temperature decreases. Such a behavior exhibited by a three $S = {}^1/_2$ spin system (rad−Cu^{II}−rad) is rather those of a magnetically independent $S = {}^1/_2$ spin. This could be explained in either of two ways, regarding which exchange coupling pathways are predominant. (i) The main magnetic interactions are the intermolecular antiferromagnetic couplings between the radicals, and what we merely observe is the paramagnetism of the central copper(II) ion. (ii) The prevalent magnetic interactions are the antiferromagnetic couplings of the copper(II) ion ($S_1 = {}^1/_2$) with the two coordinated nitroxide radicals NITPh ($S_2 \simeq S_3 = {}^1/_2$). Indeed, according to Kambe's approach,[17] and neglecting the exchange between the terminal radicals (S_2, S_3), there are for such a three-spin system (S_2−S_1−S_3) three spin states: two spin-doublet states, $S_T = {}^1/_2$ ($S_{23} = 1$), $S_T = {}^1/_2$ ($S_{23} = 0$), and one spin-quartet state, $S_T = {}^3/_2$ ($S_{23} = 1$), with the relative energy given as 0, $-2J$, and $-3J$, respectively, where $S_T = S_1 + S_2 + S_3$ and $S_{23} = S_2 + S_3$.

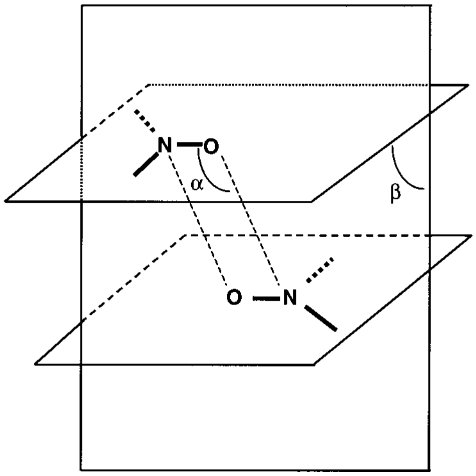
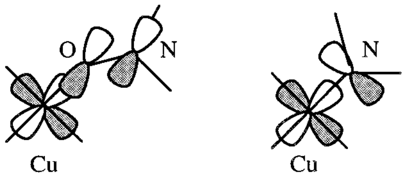


Figure 5. Geometrical parameters relevant to the magnetic interaction between the two NO groups.



(a) (b)

Figure 6. Schematic representation of the interaction between the magnetic orbital of square planar copper(II) and nitroxide radical (a) in **1** and (b) in **2**.

Moreover, the observed χT value at 300 K (0.4 emu K mol^{-1}) implies that, whatever the exchange pathway, the antiferromagnetic coupling between the magnetic centers must be a few hundred of cm^{-1}, to overcome the thermal population of the higher spin states at room temperature. This allowed us to eliminate case i. Indeed, from previous works we know that the extent of the coupling between two NO groups relies, both on the separation and on the relative orientation of their π^* orbitals[16,18−19] (Figure 5). In **1**, the intermolecular plane N2−O2−N2ii−O2ii made by the two noncoordinated NO groups, makes a β angle of 47.02° with the planes of the nitronyl nitroxide radicals (ONCNO). This arrangement of the two NO groups is unfavorable to the overlap of the π^* orbitals, which are perpendicular to the plane of the radical (ONCNO). This together with the α angle N2−O2−N2ii of 104.25°, and the large separation (O2−O2ii, 4.095(8) Å; O2−N2ii, 4.938(7) Å (ii: 1 − *x*, −*y*, *z*), are not expected to favor antiferromagnetic interaction greater than a few cm^{-1}.

On the contrary, regarding the geometrical parameters in complex **1**, a strong antiferromagnetic interaction between the central copper(II) and the two radicals is quite realistic. Indeed, the angle Cu−O4−N1 is 121.7(3)°, and the O4−N1−C3−N2−O2 mean plane containing the unpaired electron of the radical makes an angle of 86.98° with the O1−Cu−O4 plane. On the basis of previous works,[6,16] these geometrical parameters and the short distance Cu−O4 of 1.956(4) Å, favor a strong overlap of the π^* magnetic orbital of the radical with the $d_{x^2-y^2}$ magnetic orbital of the planar copper(II) ion (Figure 6). This is undoubtedly the origin of the strong antiferromagnetic copper(II)−nitroxide interaction. The coupling is strong enough that it does not allow the thermal population of the spin-quartet state $S_T = {}^3/_2$ ($S_{23} = 1$) and of the spin-doublet state $S_T = {}^1/_2$ ($S_{23} = 0$). So

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only the ground spin-doublet state $S_T = {}^1/_2$ ($S_{23} = 1$) is occupied, which means that the Cu^{II-}radical antiferromagnetic exchange interactions are greater than −500 cm^{-1}. Such strong antiferromagnetic interaction is in agreement with previous founding for copper(II)−nitroxide complexes.[20−22]

Cu(tfac)$_2$(IM2Ph)$_2$ (2). χT is 1.85 emu K mol^{-1} at 400 K and then decreases continuously to a zero value when cooling. This magnetic behavior is reminiscent of $S = {}^3/_2$ spins which are antiferromagneticaly coupled. A total spin $S = {}^3/_2$, exhibited by this other rad−Cu^{II-}rad system, means that the central copper(II) ion is ferromagneticaly coupled with both radicals. Indeed, in this case the order of the energy levels for a three-spin system S_{2}–S_{1}–S_{3} ($S_1 \simeq S_2 \simeq S_3 = {}^1/_2$) is reversed compare with the antiferromagnetic case previously describe. The ground spin state is then the spin-quartet state $S_T = {}^3/_2$ ($S_{23} = 1$), whose associated χT value (1.875 emu K mol^{-1}) corresponds to those observed for compound **2** at 380 K. As for compound **1,** this means that the magnitude of the exchange interaction must be a few hundred of cm^{-1} in order to overcome the thermal population of the higher spin states at room temperature. A strong ferromagnetic interaction is, in that case, also realistic, and it has been previously observed in copper(II) complexes of imino nitroxide.[23] Considering the molecular structure of compound **2,** the coordination of the imino nitroxide by the nitrogen atom occurs in such a way that the magnetic orbitals are rigorously orthogonal. Indeed, the copper basal plane is perpendicular to the plane Cu−N1−C3 from which the π^* orbital is perpendicular. In this geometry the overlap between the copper(II) magnetic orbital and the π^* orbital of the imino nitroxide is forbidden, but because of the short Cu−N1 bond length (1.995(4) Å) the overlap density is large. This explains the strong ferromagnetic interaction observed in **2**. A simplified scheme of the interactions between the magnetic orbitals is shown in Figure 6.

The continuous decrease of χT, which is then observed when cooling, must be attributed to the intermolecular antiferromagnetic couplings of the rad−Cu^{II}−rad complexes entities ($S_T = {}^3/_2$). Indeed, in compound **2** the shortest intermolecular distances (O2−O2I, 3.390(9) Å; O2−N2I, 3.473(7) Å (i: $1 - x, -y, -z$)) are found between the uncoordinated NO groups. Compare to compound **1** these intermolecular distances are significantly shorter, but overall the NO groups are favorably arranged in a head-to-tail geometry (Figure 7). Indeed, the plane O2−N2−C3−N1 containing the unpaired electron makes a β angle of 88.10° with the intermolecular plane N2−O2−N2i−O2i, and the α angle N2−O2−N2i is 104.25° (Figure 5). These geometrical parameters should favor a better overlap of the π^* orbitals of the radicals in compound **2,** and hence stronger intermolecular antiferromagnetic interactions than in compound **1.** This explains that for **2** one observes a decrease of χT, which was not evidenced for **1**. Moreover, because the copper(II) ion is at the inversion center, these intermolecular contacts are symmetricaly experienced, and compound **2** must be considered from the magnetic point of view as an infinite chain of weakly interacting $S = {}^3/_2$ spins. Accordingly, the temperature dependence of the magnetic susceptibility was fitted considering an infinite chain of $S = {}^3/_2$ spins antiferromagnetically coupled according to the reported equation[24,25]

$$\chi = (Ng^2\beta^2/3kT)S(S + 1)[(1 + U)/(1 - U)]$$

where $U = \coth K - 1/K$, $K = 2JS(S + 1)/kT$, $S = {}^3/_2$, and $H = -2JS_1S_2$.

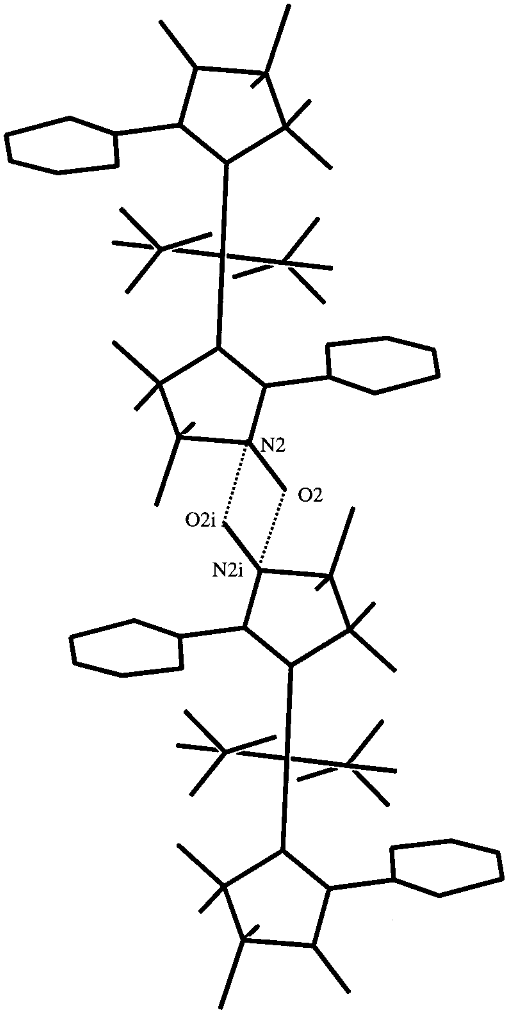

Figure 7. View showing the close contacts between the noncoordinated NO groups in **2**.

The best fit of the experimental data with this equation was obtained with $g = 2.12$ and $J = -7.1$ cm^{-1} (Figure 4). The departure of g from 2.0 accounts for both the radicals and the copper(II) ion contributions, while the exchange coupling constant is in agreement with previous values found for such an arrangement of intermolecular NO−NO contacts. To summarize, in compound **2** the central copper(II) ion is ferromagnetically coupled with both coordinated radicals. The ferromagnetic exchange interaction is so strong that at room temperature the only occupied level is the spin-state quartet $S = {}^3/_2$, which means that the copper(II)−nitroxide coupling constant is greater than +500 cm^{-1}. Due to intermolecular contacts between the uncoordinated NO groups, compounds **2** must be considered, from the magnetic point of view, as a chain of antiferromagnetically coupled $S = {}^3/_2$ spins.

Conclusions

Significant magnetic exchange interactions between spin carriers are of major concern, in view of the synthesis of compounds exhibiting spontaneous magnetization. Our present results are new examples that show how much metal−radical

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complexes can favor large magnetic exchange couplings, which may be either ferro- or antiferromagnetic, depending on the type of radical used.

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique (CNRS), the Commissariat à l'Energie Atomique (CEA), the Grenoble University Joseph Fourier (UJF), and the 3MD Network of the TMR program of the E.U. (Contract ERBFMRXCT980181).

Supporting Information Available: Crystallographic data for compounds **1** and **2**, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

IC0005590