Crystal Structure and Magnetic Properties of [Cu(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$, with 4-Me-3-Nit-trz = 2-(3-[4-Methyl-1,2,4-triazolyl])-4,4,5,5-tetramethylimidazoline-1-oxyl 3-Oxide. Intra- and Intermolecular Spin Interactions

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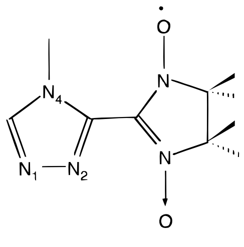
Received May 3, 1995[⊗]

The first two transition metal compounds incorporating triazole−nitronyl−nitroxide radicals as ligands have been synthesized. These compounds are [Cu(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$ (**1**) and [Ni(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$ (**2**) with 4-Me-3-Nit-trz = 2-(3-[4-methyl-1,2,4-triazolyl])-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$. The lattice parameters are $a = 9.742(2)$ Å, $b = 12.214(12)$ Å, $c = 12.981(4)$ Å, $\alpha = 67.19(4)°$, $\beta = 81.48(2)°$, and $\gamma = 79.24(4)°$, with Z = 1. The structure consists of centrosymmetrical [Cu(4-Me-3-Nit-trz)$_4$]$^{2+}$ cations and noncoordinated perchlorate anions. The Cu(II) ion is in an N$_4$O$_2$ elongated tetragonal environment with two oxygen atoms of two nitroxide groups occupying the apical positions. Within the lattice the cations form infinite chains with short intermolecular contacts involving the nitronyl−nitroxide moieties of two adjacents cations. The temperature dependence of the magnetic susceptibility and the field dependence of the magnetization at 2 K have been investigated. Both intermolecular antiferromagnetic and intramolecular ferromagnetic interactions are operative. A theoretical model has been developed to interpret quantitatively the magnetic data, which allows us to determine the values of the interaction parameters.

Introduction

We have recently initiated a new line of research dealing with the chemistry and physics of triazole−nitronyl−nitroxide radicals and transition metal compounds containing this new class of ligands.[1] The underlying idea is that the presence of triazole−nitronyl−nitroxide radicals in a compound could allow to combine two physical properties. As a matter of fact, the triazole derivatives have been extensively used as terminal and bridging ligands, and they lead to compounds exhibiting interesting magnetic properties.[2,3] They also play quite an important role in the field of spin transition compounds. Some iron(II)−1,2,4-triazole compounds present extremely abrupt transitions between low-spin and high-spin states with large thermal hystereses and well-pronounced thermochromic effects.[4−9] Some of these compounds could be utilized as active elements of display devices.[10−12] On the other hand, the simple nitronyl−nitroxide radicals are used as molecular “bricks” to design purely organic or metal organic magnets,[13−20] some of them showing extremely original structures.[21,22] Finally, the nitronyl−nitroxide radicals have also been shown to be active in nonlinear optics for second harmonic generation.[2,3]

We recently reported the synthesis, crystal structure, and magnetic properties of the first triazole−nitronyl−nitroxide radical, namely 2-(3-[4-methyl-1,2,4-triazolyl])-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide, hereafter abbreviated as 4-Me-3-Nit-trz, whose basic structure is recalled here:



This compound in the solid state exhibits intermolecular ferromagnetic interactions together with a weak ferromagnetism

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

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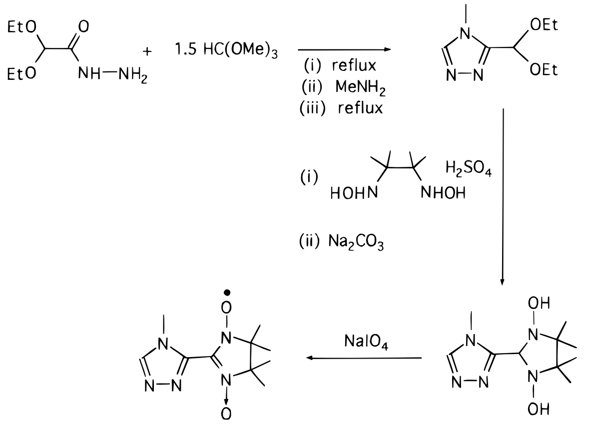

Figure 1. Three-step synthesis of the triazole−nitronyl−nitroxide radical 4-Me-3-Nit-trz.

and a spontaneous magnetization below $T_c = 0.60$ K. A preliminary polarized neutron diffraction investigation has revealed that a nonnegligible negative spin density is located in the vicinity of the nitrogen atom occupying the 1-position of the triazole ring, i.e. the nitrogen atom which is the farthest from the nitroxide groups. In contrast, the spin densities on the nitrogen atoms occupying the 2- and 4-position are negligibly small.[1]

In this paper we report on the first compounds in which 4-Me-3-Nit-trz plays the role of a ligand. These compounds are [Cu(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$ (**1**) and [Ni(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$ (**2**). We will describe the synthesis and the crystal structure of **1** and then discuss its unusual magnetic properties that result from a combination of intra- and intermolecular interactions. A theoretical model that accounts for the magnetic data was developed for **1** and will be presented, along with a brief description of the magnetic properties of **2**.

Experimental Section

Synthesis. The triazole−nitronyl−nitroxide radical 4-Me-3-Nit-trz was synthesized in three steps according to the scheme of Figure 1. The detail of this synthesis was described elsewhere.[1] The title compound **1** was prepared as follows: 1.01 g (4.24 × 10^{-3} mol) of 4-Me-3-Nit-trz was dissolved in 150 mL of hot methanol, and the solution was filtered. Then 0.412 g (1.11 × 10^{-3} mol) of $Cu(ClO_4)_2\cdot 6H_2O$ dissolved in 5 mL of methanol was added, and the solution turned from red to dark violet. Well-shaped single crystals appeared within 24 h. They were isolated, washed with methanol, and dried, yielding 1.23 g of [Cu(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$. Anal. Calcd for $C_{40}H_{64}N_{20}O_{16}Cl_2Cu$ (**1**): C, 39.53; H, 5.31; N, 23.05; Cl, 5.83; Cu, 5.20. Found: C, 39.81; H, 5.21; N, 22.73; Cl, 6.34; Cu, 5.10.

The nickel derivative [Ni(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$ (**2**) was synthesized in a similar way, $Ni(ClO_4)_2\cdot 6H_2O$ replacing $Cu(ClO_4)_2\cdot 6H_2O$, except that the compound did not precipitate. Needle-shaped violet-black single crystals were obtained by slow evaporation of the solvent. Unfortunately, these crystals were too small for a structure determination. Anal. Calcd for $C_{40}H_{64}N_{20}O_{16}Cl_2Ni$ (**2**): C, 39.68; H, 5.33; N, 23.14; Cl, 5.86; Ni, 4.85. Found: C, 39.43; H, 5.22; N, 22.23; Cl, 5.85, Ni, 4.96.

Table 1. Crystallographic Data for [Cu(4-Me-3-Nit-trz)$_4$)](ClO$_4$)$_2$ (**1**)

chem formula: $C_{40}H_{64}N_{20}O_{16}Cl_2Cu$	fw = 1215.53
$a = 9.742(2)$ Å	space group = $P\bar{1}$ (No. 2)
$b = 12.214(9)$ Å	T = 23 °C
$c = 12.981(4)$ Å	$\lambda = 0.71073$ Å
$\alpha = 67.19(4)$ °	$\rho_{calcd} = 1.448$ g cm^{-3}
$\beta = 81.48(2)$ °	$\mu = 5.667$ cm^{-1}
$\gamma = 79.24(4)$ °	$R(F_o)^a = 0.039$
$V = 1394(1)$ Å^3	$R_w(F_o)^b = 0.055$
$Z = 1$	

^{a} $R(F_o) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w(F^o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$; $w = 4F_o^2/[\sigma^2(I) + (0.07F_o^2)^2]$.

Crystallographic Data Collection and Structure Determination. The X-ray data collection was performed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centered reflections. The data were collected with the ω-scan method. Three standard reflections were measured every hour and revealed no fluctuation in intensities. These intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods and successive Fourier difference syntheses. An empirical absorption correction was applied using the DIFABS procedure.[24a] The refinements were performed by the full-matrix least-squares method. The hydrogen atoms, both those found by Fourier synthesis and those placed at computed positions, were not refined. The scattering factors were taken from ref 24b. All the calculations were performed on a MicroVax 3100 using the Molen program.[25]

The crystallographic data are summarized in Table 1, and the atomic coordinates of non-hydrogen atoms are given in Table 2.

Magnetic Measurements. These were carried out with a Quantum Design SQUID magnetometer working down to 1.7 K and up to 50 kOe. The data were corrected for the diamagnetism of the core estimated as 550 × 10^{-6} cm^3 mol^{-1} for both **1** and **2**.

EPR Spectra. These were recorded on powder samples at various temperatures down to 4.2 K with a Bruker ER 200 spectrometer working in the X-band region.

Description of the Structure of 1

The structure consists of [Cu(4-Me-3-Nit-trz)$_4$]$^{2+}$ cations and noncoordinated perchlorate anions. A view of the cation is given in Figure 2. The copper atom is located on an inversion center, in a 4 + 2 environment. The basal plane is made of four nitrogen atoms, two of them occupying the 1-position and the other two the 2-position of the four triazole rings. The corresponding Cu−N basal bond lengths are 1.987(2) and 2.038(2) Å, respectively. The two apical positions are occupied by nitroxide oxygen atoms of the radicals also linked to the metal ion through the triazole 2-position. The Cu−O apical bond length is 2.385(2) Å.

Another way to describe the structure of [Cu(4-Me-3-Nit-trz)$_4$]$^{2+}$ is to say that two ligands noted rad$_1$ and rad$_1^{i}$ are terminal; they are coordinated to the metal through the nitrogen atom occupying the 1-position of the triazole ring. The other two ligands noted rad$_2$ and rad$_2^{i}$ are chelating; they are coordinated to the metal through the nitrogen atom occupying the 2-position of the triazole ring and the oxygen atom of one of the N−O groups. The dihedral angle between the triazole mean plane and the ONC(sp^2)NO mean plane within the same ligand is equal to 50.5(2)° for rad$_1$ and 28.5(3)° for rad$_2$. For the free radical the value of this dihedral angle has been found as 59.2°.[1] Therefore, the chelating radical is much more tilted

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Table 2. Positional Parameters for the Non-Hydrogen Atoms of $[Cu(4\text{-}Me\text{-}3\text{-}Nit\text{-}trz)_4](ClO_4)_2$ (**1**)

atom	*x*	*y*	*z*	B^a (Å^2)
Cu	0.000	0.000	0.000	2.025(9)
C1	0.78844(8)	0.06222(6)	0.60553(6)	3.53(2)
O1	0.1272(2)	−0.0200(2)	−0.1650(2)	2.99(4)
O2	0.1021(2)	0.3865(2)	−0.3758(2)	4.30(6)
O3	0.4310(2)	0.3976(2)	−0.1247(2)	4.71(6)
O4	−0.0470(2)	0.5156(2)	−0.1156(2)	3.72(5)
O5	0.7135(3)	0.1189(3)	0.5090(2)	7.74(9)
O6	0.7118(3)	0.0981(2)	0.6938(2)	5.48(7)
O7	0.9213(3)	0.1008(3)	0.5851(3)	7.57(9)
O8	0.7959(4)	−0.0637(2)	0.6420(3)	7.6(1)
N1	−0.1124(2)	0.1291(2)	−0.1157(2)	2.18(5)
N2	−0.2495(2)	0.1701(2)	−0.0919(2)	2.98(5)
N3	−0.1781(3)	0.2875(2)	−0.2615(2)	2.82(5)
N4	0.1579(2)	0.0813(2)	−0.2377(2)	2.40(5)
N5	0.1441(2)	0.2739(2)	−0.3399(2)	2.77(5)
N6	0.1073(2)	0.1264(2)	0.0038(2)	2.21(5)
N7	0.0902(2)	0.2444(2)	−0.0707(2)	2.36(5)
N8	0.2381(2)	0.2239(2)	0.0506(2)	2.55(5)
N9	0.3120(2)	0.4650(2)	−0.1373(2)	2.90(5)
N10	0.0839(2)	0.5193(2)	−0.1379(2)	2.43(5)
C1	−0.2851(3)	0.2628(3)	−0.1801(3)	3.41(7)
C2	−0.1920(4)	0.3757(3)	−0.3756(3)	4.70(9)
C3	−0.0703(3)	0.2006(2)	−0.2174(2)	2.15(5)
C4	0.0724(3)	0.1867(2)	−0.2676(2)	2.31(5)
C5	0.3071(3)	0.0959(2)	−0.2849(2)	2.80(6)
C6	0.3723(4)	−0.0070(3)	−0.3227(3)	4.38(8)
C7	0.3832(3)	0.0926(3)	−0.1884(3)	3.96(8)
C8	0.2844(3)	0.2220(2)	−0.3810(2)	3.15(7)
C9	0.2641(4)	0.2185(3)	−0.4930(3)	5.3(1)
C10	0.3924(4)	0.3038(3)	−0.3950(3)	4.9(1)
C11	0.1957(3)	0.1171(2)	0.0750(2)	2.57(6)
C12	0.3305(3)	0.2519(3)	0.1138(3)	4.12(7)
C13	0.1702(3)	0.3006(2)	−0.0408(2)	2.23(5)
C14	0.1872(3)	0.4265(2)	−0.1020(2)	2.30(5)
C15	0.2967(3)	0.5998(2)	−0.1859(3)	3.06(7)
C16	0.4092(4)	0.6421(3)	−0.2790(3)	5.01(9)
C17	0.3097(4)	0.6371(3)	−0.0877(3)	4.58(8)
C18	0.1445(3)	0.6297(2)	−0.2217(2)	2.71(6)
C19	0.0629(4)	0.7438(3)	−0.2115(3)	4.61(9)
C20	0.1346(4)	0.6269(3)	−0.3359(3)	4.94(9)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

then the terminal one with respect to the uncoordinated triazole−nitronyl−nitroxide molecule. This tilt allows the nitroxide oxygen atom of the chelating radical to occupy an apical position in the copper coordination sphere.

The $[Cu(4\text{-}Me\text{-}3\text{-}Nit\text{-}trz)_4]^{2+}$ cations pack within the crystal lattice in such a way that they form infinite chains running along the *b* direction, as shown in Figure 3. Two adjacent cations along a chain are related through an inversion center situated between the nitronyl−nitroxide rings of two terminal radicals. The Cu- - -Cu(x, $1 + y$, z) separation is as large as 12.214(12) Å. On the other hand, the shortest intermolecular interaction is O4- - -N10^i(x, $1 + y$, z) = 3.124(3) Å, and involves atoms belonging to nitroxide groups. The corresponding O4- - -O4^i-(x, $1 + y$, z) and N10- - -N10^i(x, $1 + y$, z) separations are equal to 3.130(4) and 3.600(3) Å, respectively. Those chains are well separated from each other by the perchlorate anions.

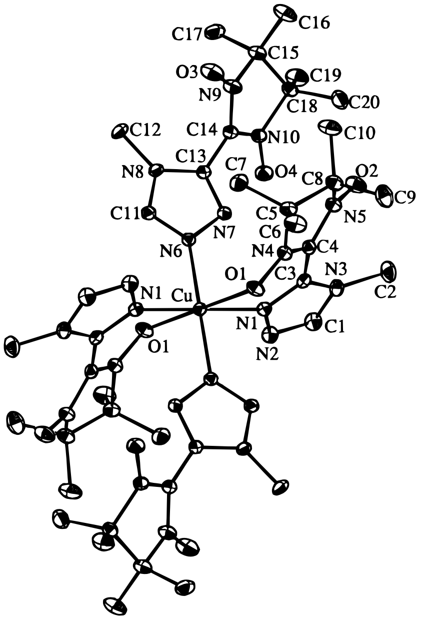

Figure 2. View of the $[Cu(4\text{-}Me\text{-}3\text{-}Nit\text{-}trz)_4)]^{2+}$ cation showing the atom labeling scheme along with the thermal vibration ellipsoids.

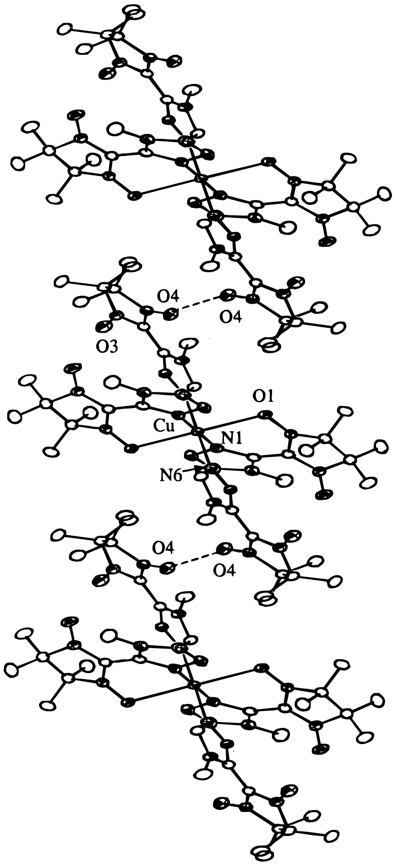

Figure 3. View of the chains of $[Cu(4\text{-}Me\text{-}3\text{-}Nit\text{-}trz)_4)]^{2+}$ cations running along the *b* direction.

Magnetic Properties

$[Cu(4\text{-}Me\text{-}3\text{-}Nit\text{-}trz)_4](ClO_4)_2$ (1). The magnetic susceptibility data are shown in Figure 4 in the form of the $\chi_M T$ vs T plot, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature, $\chi_M T$ is equal to 1.92 cm^3 K mol^{-1}, which roughly corresponds to what is expected for five isolated $^1/_2$ local spins, one arising from the Cu(II) ion, the other four from the radicals. As T is lowered, $\chi_M T$ first decreases, reaches a minimum value equal to 1.52 cm^3 K mol^{-1} around 35 K, then slightly increases as T is lowered further down to 10 K. At that temperature $\chi_M T$ is equal to 1.62 cm^3 K mol^{-1}. When the sample is cooled down below 10 K, $\chi_M T$ decreases again. The profile of this $\chi_M T$ vs T curve is rather unusual and reveals both antiferro (in the 35−250 K temperature range) and ferromagnetic (in the 10−35 K temperature range) interactions.

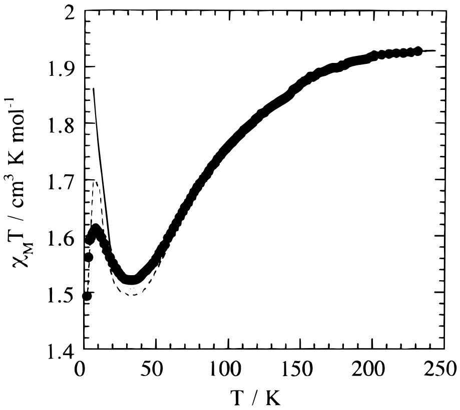

Figure 4. $\chi_M T$ vs T curve for [Cu(4-Me-3-Nit-trz)$_4$](ClO$_4$)$_2$ (**1**). Key: (●) experimental data; (—) calculated curve with the first model taking into account the rad$_1$- - -rad$_1{}^i$ and Cu—rad$_2$ interactions; (- - -) calculated curve with the second model taking into account an effective interaction between the rad$_2$—Cu-rad$_2{}^i$ triads (see text).

A careful look at the crystal structure allows to assign the two kinds of interaction. The short intermolecular contacts between the nitronyl—nitroxide moieties of the terminal radicals rad$_1$ and rad$_1{}^i$ along the chain should give rise to a large antiferromagnetic interaction. Indeed, these contacts lead to an overlap of the π^* singly-occupied orbitals associated with the nitronyl nitroxide groups. On the other hand, the intramolecular interaction between the Cu(II) ion and a nitroxide group in the apical position is expected to be weakly ferromagnetic. Indeed, this interaction involves orthogonal magnetic orbitals.[13]

Two other interactions might play a certain role in the magnetic behavior. (i) The first is the intramolecular interaction between the Cu(II) ion and the terminal radical rad$_1$ occurring through the triazole ring. This interaction is probably very weak owing to the large separation between the Cu(II) ion and the N—O groups of rad$_1$ (Cu- - -N9 = 6.455(2) Å, Cu- - -O3 = 6.583(2) Å, Cu- - -N10 = 6.067(2) Å, Cu- - -O4 = 5.824(2) Å.). (ii) The second is the through-space intramolecular interaction between rad$_1$ and rad$_2$. Again, this interaction may be anticipated to be very weak, the relevant separations between oxygen atoms of the nitronyl groups being as large as O2- - -O3 = 4.951(4) Å and O2- - -O4 = 4.222(4) Å.

Let us now attempt to interpretate quantitatively the magnetic susceptibility data. For that let J_1 and J_2 stand for the rad$_1$- - -rad$_1{}^i$and Cu-rad$_2$ interaction parameters, respectively. As a first approximation, we neglect the Cu—rad$_1$ and rad$_1$- - -rad$_2$ interactions (throughout the paper the notations A—B and A- - -B are used for through-bond and through space interaction, respectively). The zero-field interaction Hamiltonian may then be expressed as

$$H = -J_1\mathbf{S}_{\mathrm{rad}_1}\cdot\mathbf{S}_{\mathrm{rad}_1{}^i} - J_2\mathbf{S}_{\mathrm{Cu}}\cdot(\mathbf{S}_{\mathrm{rad}_2} + \mathbf{S}_{\mathrm{rad}_2{}^i}) \quad (1)$$

and the magnetic susceptibility as[26]

$$\chi_M T = (\chi_M T)_P + (\chi_M T)_T \quad (2)$$

where the first term in the right-hand side of (1) and (2) refers to the rad$_1$- - -rad$_1{}^i$ pair, and the second term to the rad$_2$—Cu—rad$_2{}^i$ triad, with

$$(\chi_M T)_P = 2Ng_{\mathrm{rad}}{}^2\beta^2/[k(3 + \exp(-J_1/kT)] \quad (3)$$

$$(\chi_M T)_T = (N\beta^2/4k)[10g_{3/2,1}{}^2 + g_{1/2,0}{}^2\exp(-J_2/2kT) + g_{1/2,1}{}^2\exp(-3J_2/2kT)]/[2 + \exp(-J_2/2kT) + \exp(-3J_2/2kT)] \quad (4)$$

and

$$g_{1/2,1} = (4g_{\mathrm{rad}} - g_{\mathrm{Cu}})/3$$
$$g_{1/2,0} = g_{\mathrm{Cu}}$$
$$g_{3/2,1} = (2g_{\mathrm{rad}} + g_{\mathrm{Cu}})/3 \quad (5)$$

The $g_{S,S'}$ terms refer to the Zeeman factors of the low-lying states of the triad, and g_{rad} and g_{Cu} to the local Zeeman factors for the radical and the Cu(II) ion, repectively. In (1) and (4) the interaction between the rad$_2$ and rad$_2{}^i$ ligands through the metal ion is neglected. An excellent agreement between experimental and calculated data above 20 K is observed for $J_1 = -103$ cm^{-1}, $J_2 = 14.3$ cm^{-1}, $g_{\mathrm{rad}} = 2.00$ and $g_{\mathrm{Cu}} = 2.10$. The agreement factor defined as $\sum[(\chi_M T)^{\mathrm{cal}} - (\chi_M T)^{\mathrm{obs}}]^2/\sum[(\chi_M T)^{\mathrm{obs}}]^2$ is then equal to 2×10^{-5}.

The model developed above does not account for the decrease of $\chi_M T$ as T is lowered below ca. 10 K. This low-temperature behavior is too pronounced to be attributed to the zero-field splitting within the $S = {}^3/_2$ ground state of the rad$_2$—Cu—rad$_2{}^i$ triad, and most likely reflects the combined effect of the Cu—rad$_1$ and rad$_1$- - -rad$_2$ interactions. What is important concerning the role of these interactions, it is that they lead to an antiparallel alignment of the S_T triad spins *whatever their respective signs may be*. This situation is emphasized in Figure 5 where J_3 stands for the interaction parameter between rad$_1$ and the rad$_2$—Cu—rad$_2{}^i$ triad. It follows that in the low-temperature range the effect of J_3 may be described by an effective antiferromagnetic interaction between the S_T triad spins along the chain, with an exchange Hamiltonian of the form

$$H_{\mathrm{chain}} = -J_{\mathrm{eff}}\sum_i \mathbf{S}_{\mathrm{T}_i}\cdot\mathbf{S}_{\mathrm{T}_{i+1}} \quad (6)$$

where J_{eff} stands for the effective interaction parameter between the triad spins along the chain, S_T being temperature dependent.[27-29] The product magnetic susceptibility by temperature of such a chain of S_T triad spins, denoted as $(\chi_M T)_{\mathrm{T\,chain}}$, may then be expressed using the classical-spin chain model derived by Fisher,[30] which leads to

$$(\chi_M T)_{\mathrm{T\,chain}} = (Ng_{\mathrm{T}}{}^2\beta^2/3k)[S_T(S_T + 1)][(1 + u)/(1 - u)]$$
$$u = \coth[J_{\mathrm{eff}}S_T(S_T + 1)/kT] - kT/[J_{\mathrm{eff}}S_T(S_T + 1)] \quad (7)$$

where g_T stands for the Zeeman factor of the triad spin, taken equal to 2.00. This triad spin S_T may be defined as

$$S_T(S_T + 1) = 3k(\chi_M T)_T/Ng_T{}^2\beta^2 \quad (8)$$

In this second model $\chi_M T$ is expressed as in eq 2 except that $(\chi_M T)_T$ is replaced by $(\chi_M T)_{\mathrm{T\,chain}}$. The least-squares fitting of the data in the whole temperature range leads to $J_{\mathrm{eff}} = -0.24$

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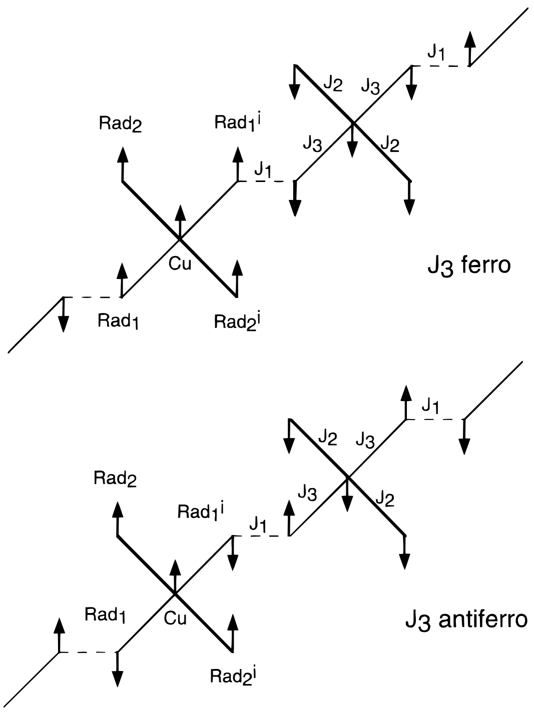

Figure 5. Spin topology in the chain of $[Cu(4-Me-3-Nit-trz)_4)]^{2+}$ cations (see text).

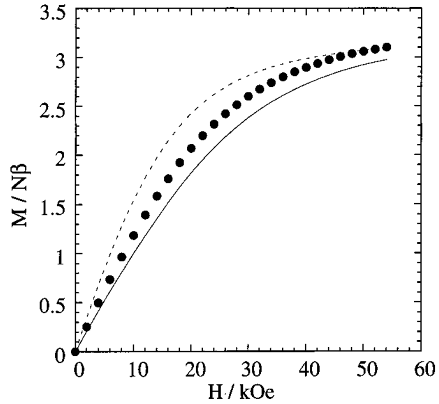

Figure 6. Field dependence of the magnetization at 2 K for $[Cu(4-Me-3-Nit-trz)_4](ClO_4)_2$ (**1**). Key: (●) experimental data, (- - -) Brillouin function for a $S = {}^3/_2$ spin; (—) Brillouin function for three isolated $^1/_2$ spins.

cm^{-1}. The agreement factor is then equal to 2×10^{-4}, i.e. 1 order of magnitude higher than with the former model. In other words our second model qualitatively accounts for the maximum of $\chi_M T$ around 10 K. However, it does not provide an accurate description of the experimental data nor allows us to determine the sign of J_3.

The field dependence of the magnetization measured at 2 K is shown in Figure 6. The magnetization reaches a saturation value of ca. 3Nβ, which exactly corresponds to three aligned $^1/_2$ spins. At that temperature the spins of the terminal radicals rad_1 and $rad_1{}^i$ are entirely cancelled by the strong rad_1- - -$rad_1{}^i$ intermolecular interaction. The experimental magnetization data are sligthly below the Brillouin function for a spin $S = {}^3/_2$, which confirms that a weak interaction described by J_{eff} couples antiferromagnetically the S_T triad spins. On the other hand, these magnetization data are above the Brillouin function for three isolated $^1/_2$ spins.

The X-band EPR spectra of a powder sample of **1** are not much informative. They show an almost symmetrical single line centered at $g = 2.00$, with a line width of 290 G.

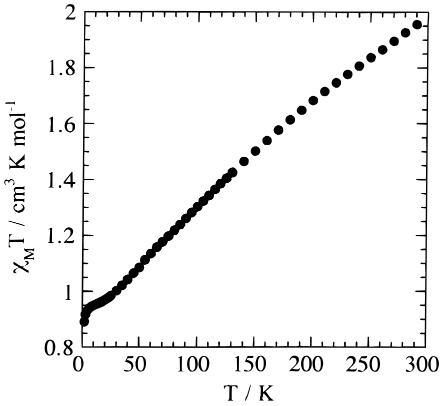

Figure 7. $\chi_M T$ vs T curve for $[Ni(4-Me-3-Nit-trz)_4](ClO_4)_2$ (**2**).

$[Ni(4-Me-3-Nit-trz)_4](ClO_4)_2$ (2). The $\chi_M T$ vs T curve for **2** is shown in Figure 7. This curve is much simpler than than for **1**. At room temperature, $\chi_M T$ is equal to 2.0 cm^3 K mol^{-1}, which is already less than expected for four $S_{rad} = {}^1/_2$ and one $S_{Ni} = 1$ local spins. As T is lowered, $\chi_M T$ decreases, then reaches a plateau in the 5−30 K temperature range with $\chi_M T = 1.0$ cm^3 K mol^{-1}, and finally decreases again as T is lowered further below ca. 5 K. The $\chi_M T$ value for the plateau corresponds to what is anticipated for the $S_{Ni} = 1$ local spin. Therefore, large intermolecular antiferromagnetic interactions most likely cancel the radical spins in the low temperature range, and only the S_{Ni} spin is retained. The spin triplet ground state is split in zero field, which results in the decrease of $\chi_M T$ observed at very low temperature.[26] Such an interpretation implicitly supposes that the intramolecular interactions between the Ni(II) ions and the ligands are very small as compared to the intermolecular interactions. In the absence of structural information, we cannot go further in the interpretation of the magnetic data.

Discussion and Conclusion

The compounds **1** and **2** are the very first in which a triazole−nitronyl−nitroxide radical is bound to a metal ion. The crystal structure of **1** provides important insight on the coordination modes for this type of ligands. Actually, five possibilities could be encountered: namely, (i) the monodentate coordination through the triazole N1 atom; (ii) the monodentate coordination through the triazole N2 atom, N1 and N2 referring to the nitrogen atoms occupying the 1- and 2-position of the triazole ring, respectively; (iii) the bidentate coordination through N2 and the oxygen atom of one of the nitroxide groups; (iv) the monodentate coordination through the oxygen atom of one of the nitroxide groups; (v) the bridging coordination through the oxygen atoms of the two nitroxide groups. In **1** both situations i and iii are realized. We are presently exploring the possibilities to realize the other coordination modes. In **2**, probably, only situation i is realized; if so, the nitronyl−nitroxide moieties are located at the periphery of the $[Ni(4-Me-3-Nit-trz)_4]^{2+}$ cation, which is in line with the canceling of the radical spins at low temperature, owing to short intermolecular contacts. In $[Cu(4-Me-3-Nit-trz)_4]^{2+}$ the Cu(II) ion has a rather classical 4 + 2 environment. In $[Ni(4-Me-3-Nit-trz)_4]^{2+}$ the Ni(II) ion should have a tetrahedral environment, which would agree with the paramagnetism of the metal ion.

It was worth investigating in detail the magnetic behavior of **1**. The magnetic behavior exhibited in the crystal lattice of **1** by the $[Cu(4-Me-3-Nit-trz)_4]^{2+}$ cation corresponds to a five $^1/_2$ spin system, and a careful examination of the crystal structure suggests that the intermolecular interactions should play a role.

Despite the complexity of the problem, the combination of magnetic susceptibility vs temperature and magnetization vs field measurements allowed us to interpret unambigously the magnetic properties. The magnetization curve at 2 K learns us that two out of five $^1/_2$ spins are cancelled, and the examination of the structure allows us to attribute this spin canceling to intermolecular interactions involving the rad_1 and $\mathrm{rad}_1{}^{\mathrm{i}}$ radicals. The magnetic susceptibility data indicate that the $^1/_2$ spins within the rad_2−Cu−$\mathrm{rad}_2{}^{\mathrm{i}}$ triad are ferromagnetically coupled. A theoretical model was developed, which led to the values of the antiferromagnetic intermolecular and ferromagnetic intramolecular interaction parameters. These values agree with those found in other compounds in which simpler nitronyl−nitroxide radicals are coordinated to a Cu(II) ion.[13]

Two interactions have not been evaluated quantitatively, namely Cu−rad_1 and rad_1- - -rad_2. Whatever their respective signs may be, they favor an antiparallel alignment of the rad_2−Cu−$\mathrm{rad}_2{}^{\mathrm{i}}$ triad spins. The Cu−rad_1 interaction might be weakly ferromagnetic in nature, according to the McConnell mechanism.[31−33] Indeed, a preliminary polarized neutron diffraction study concerning the free radical has revealed a significant negative spin density on the nitrogen atom occupying the 1-position of the triazole ring. In the present case, this nitrogen atom, N6, is directly linked to the metal.

We are presently pursuing our endeavors dealing with triazole−nitronyl−nitroxide radicals. In a near future we will report the very interesting magnetic properties of 5-Me-3-Nit-trz, the isomer of 4-Me-3-Nit-trz where the methyl substituent is displaced from the 4- to the 5-position, and then on other transition metal compounds containing this class of ligands.

Acknowledgment. We are very grateful to the European Union for its financial support in the frame of the Human Capital and Mobility Program, Contract No. ERBCHRXCT920080. A.L. would like to thank the Ultimatech Program from the CNRS for a post-doctoral fellowship.

Supporting Information Available: Tables SI−SIV listing the detailed crystallographic data, atomic coordinates and isotropic temperature factors for the hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

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