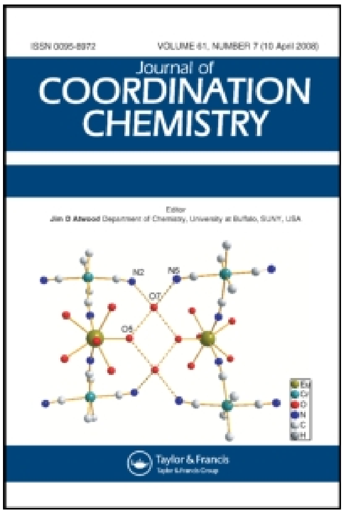

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Syntheses, crystal structures and magnetic properties of a new thienyl-substituted nitronyl nitroxide and its copper(II) complex

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Syntheses, crystal structures and magnetic properties of a new thienyl-substituted nitronyl nitroxide and its copper(II) complex

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A new building block for molecule-based magnetic materials – thiophene-substituted nitronyl nitroxide, NIT2-thp, [**1**, NIT2-thp = 4,4,5,5-tetramethyl-2-(thiophenal-2-yl)imidazoline-1-oxyl-3-oxide] and its copper(II) complex $[Cu(hfac)_2]_3(NIT2\text{-}thp)_2$ (**2**) (hfac = hexafluoroacetylacetonate) have been synthesized and characterized structurally and magnetically. For **1**, dimers were formed and arranged through intermolecular interactions, the shortest contact between nitroxide groups is 4.115 Å among adjacent dimers. In **2** two types of copper interaction with **1** give three colinear Cu(II) ions linked by two μ-1,4 bridging nitroxide ligands. The central metal ion is in a distorted octahedron, axially coordinated by two nitroxide oxygen atoms, while the two external metal ions are in distorted square-pyramidal environments with the nitroxide oxygen atom coordinated in the basal plane. Magnetic susceptibility data for **1** and **2** have been measured in the range 3–300 K. There are antiferromagnetic interactions ($J = -3.89\,\mathrm{cm^{-1}}$) between the dimers of **1** and also ferromagnetic interactions in **2**. The magnetic properties of **1** and **2** are discussed in connection with their crystal structures.

Keywords: Trinuclear copper(II) complex; Nitronyl nitroxide; Crystal structures; Magnetic interactions

1. Introduction

Nitronyl nitroxide radicals (NITR) have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [1–4], due to their exceptional stability and rich chemistry. The nitroxide derivatives can be bound to the metal through the oxygen of O–N groups, resulting in a good variety of transition metal-radical complexes [5–10].

Although the family of nitronyl nitroxides, such as NITR (R = methyl, ethyl, phenyl, pyridyl etc.), has been widely studied, thiophenalyl substituents have rarely been reported. Few trinuclear copper complexes containing nitroxides are reported in the

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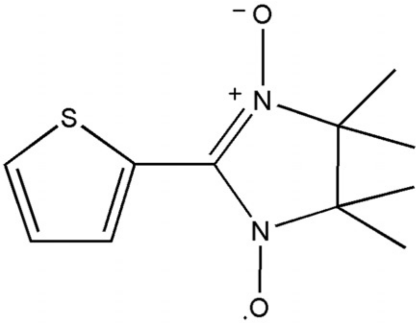

Scheme 1. NIT2-thp.

literature [11–13]. Therefore, in order to extend our knowledge of the extremely rich chemistry of such systems and explore new building blocks for molecule-based magnetic materials, we have synthesized a new thiophene-substituted nitronyl nitroxide radical and a trinuclear copper(II) complex containing this radical ligand. We will describe the syntheses of the new nitroxide NIT2-thp (**1**) (scheme 1) and its trinuclear copper(II) complex $[Cu(hfac)_2]_3(NIT2\text{-}thp)_2$ (**2**), the crystal structures, and the magnetic properties of **1** and **2**.

2. Experimental

2.1. *General*

All reagents were of analytical grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Vario EL III elemental analyzer. The infrared spectrum of a KBr pellet was recorded in the range 4000–600 cm^{-1} on an Avatar^{TM} 360 E.S.P. IR spectrometer. Variable-temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. *Preparation of NIT2-thp (1) and [Cu(hfac)$_2$]$_3$(NIT2-thp)$_2$ (2)*

Compound **1** was prepared according to a literature method [14]. Anal. Calcd (%) for **1**, $C_{11}H_{15}N_2O_2S$: C, 55.20; H, 6.32; N, 11.71. Found (%): C, 55.25; H, 6.30; N, 11.73. IR (KBr disc) $\nu_{N\text{–}O}$ (cm^{-1}) 1368. Complex **2** was synthesized as follows: a mixture of $Cu(hfac)_2 \cdot 2H_2O$ (52 mg, 0.1 mmol) and NIT2-thp (24 mg, 0.1 mmol) was dissolved with heating to 65°C in heptane/acetone (10 mL/10 mL) and the resulting solution was stirred for 1 h and then cooled to room temperature. After filtration, the filtrate was allowed to stand at room temperature for 72 h to produce well-shaped dark green crystals of **2**. Anal. Calcd (%) for **2**, $C_{52}H_{36}F_{36}Cu_3N_4O_{16}S_2$: C, 32.67; H, 1.90; N, 2.93. Found (%): C, 32.76; H, 1.88; N, 2.95.

Table 1. Crystal data and details of experiment for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{11}H_{15}N_2O_2S$	$C_{52}H_{36}F_{36}Cu_3N_4O_{16}S_2$
Formula weight	239.31	1911.59
Temperature (K)	291(2)	291(2)
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	23.778(5)	9.3695(10)
b	8.4354(18)	13.2974(14)
c	12.308(3)	16.2987(17)
α		107.116(2)
β	103.446(4)	98.657(2)
γ		100.937(2)
Volume, Z (Å^3)	2401.1(9), 8	1858.8(3), 1
Calculated density (Mg m^{-3})	1.324	1.708
Absorption coefficient (mm^{-1})	0.257	1.059
$F(000)$	1016	947
Crystal size (mm^3)	$0.29 \times 0.25 \times 0.24$	$0.49 \times 0.30 \times 0.30$
θ range for data collection (°)	2.57–27.50	2.27–25.50
Limiting indices	$-30 \le h \le 28$, $-10 \le k \le 10$, $-15 \le l \le 14$	$-11 \le h \le 11$, $-16 \le k \le 15$, $-9 \le l \le 19$
Reflections collected	7023	10098
Independent reflection	2753 [($R_{int} = 0.0795$)]	6793 [($R_{int} = 0.0102$)]
Data/restraints/parameters	2753/0/149	6793/636/562
Goodness-of-fit on F^2	1.602	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1272$, $wR_2 = 0.3828$	$R_1 = 0.0570$, $wR_2 = 0.1704$
R indices (all data)	$R_1 = 0.1555$, $wR_2 = 0.4182$	$R_1 = 0.0663$, $wR_2 = 0.1820$
Largest diff. peak and hole (e Å^{-3})	2.146 and −1.052	0.861 and −0.665

2.3. *Crystal structure determination*

Blue single crystal of **1** with dimensions 0.29 mm × 0.25 mm × 0.24 mm and green single crystal of **2** with dimensions 0.49 mm × 0.30 mm × 0.30 mm were put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-α radiation ($\lambda = 0.71073$ Å) by using ω–2θ scan technique at room temperature. A total of 7023 reflections were collected for **1** and 10098 for **2**, of which 2753 ($R_{int} = 0.0795$) and 6793 ($R_{int} = 0.0102$) were independent for **1** and **2** in the ω–2θ range of 2.57–27.50° and 2.27–25.50°, and 1858 and 5588 observed reflections with $I > 2\sigma(I)$ were used for structure refinements for **1** and **2**, respectively. The structures were solved by direct methods with SHELXS-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. The final agreement factor values are $R = 0.1272$ and $wR = 0.3828$ ($w = 1/[\sigma^2(F_o)^2 + (0.2000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3)$, $S = 1.602$, $(\Delta\sigma)_{max} = 0.000$. $(\Delta\rho)_{max} = 2.146$ and $(\Delta\rho)_{mix} = -1.052$ e Å^{-3} for **1**. The final agreement factor values are $R = 0.0570$ and $wR = 0.1704$ ($w = 1/[\sigma^2(F_o)^2 + (0.1122P)^2 + 1.6483P]$, where $P = (F_o^2 + 2F_c^2)/3)$, $S = 1.068$, $(\Delta\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.861$ and $(\Delta\rho)_{mix} = -0.665$ e Å^{-3} for **2**. A summary of the crystallographic data for **1** and **2** is given in table 1. Selected bond lengths and angles are illustrated in table 2 for **1** and **2**.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
S(1)–C(1)	1.596(8)	N(1)–C(6)	1.484(6)
S(1)–C(4)	1.684(5)	N(2)–C(5)	1.335(6)
O(1)–N(1)	1.285(5)	N(1)–C(5)	1.359(6)
O(2)–N(2)	1.282(5)	C(4)–C(5)	1.426(6)
C(1)–S(1)–C(4)	93.8(3)	O(1)–N(1)–C(5)	125.3(4)
O(1)–N(1)–C(6)	121.7(4)	C(5)–N(1)–C(6)	112.8(4)
O(2)–N(2)–C(5)	125.4(4)	O(2)–N(2)–C(7)	121.1(4)
C(5)–N(2)–C(7)	112.9(4)	N(2)–C(5)–N(1)	108.5(4)
N(1)–C(5)–C(4)	125.4(4)	N(2)–C(5)–C(4)	126.1(4)
C(5)–C(4)–S(1)	122.2(4)	C(5)–C(4)–C(3)	122.8(4)
2			
Cu(1)–O(4)	1.931(3)	Cu(1)–O(4)#1	1.931(3)
Cu(1)–O(3)	1.938(3)	Cu(1)–O(3)#1	1.938(3)
Cu(1)–O(1)	2.512(3)	Cu(2)–O(5)	1.921(3)
Cu(2)–O(7)	1.925(3)	Cu(2)–O(2)	1.944(3)
Cu(2)–O(8)	1.968(3)	Cu(2)–O(6)	2.225(3)
O(1)–N(1)	1.272(4)	O(2)–N(2)	1.301(4)
N(1)–C(5)	1.345(5)	N(2)–C(5)	1.344(5)
O(5)–Cu(2)–O(7)	174.07(13)	O(2)–Cu(2)–O(8)	164.89(14)
O(8)–Cu(2)–O(6)	87.94(14)	O(5)–Cu(2)–O(6)	89.02(13)
N(2)–O(2)–Cu(2)	123.5(2)	N(1)–O(1)–Cu(1)	150.7(3)
O(1)#1–Cu(1)–O(1)	180.0	O(4)#1–Cu(1)–O(4)	180.0
O(3)#1–Cu(1)–O(3)	180.0	O(4)–Cu(1)–O(1)	97.23(11)
O(3)–Cu(1)–O(1)	92.42(12)	O(3)#1–Cu(1)–O(1)	87.58(12)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z$.

3. Results and discussion

3.1. *Crystal structure of (1)*

The crystal structure of **1** is shown in figure 1. As for most nitronyl nitroxide derivatives, the N1–O1 and N2–O2 bond lengths are almost the same, 1.285(5) Å and 1.282(5) Å, respectively, due to the fact that the unpaired electron is delocalized over the O–N–C–N–O unit. This is also shown for N1–C5 and N2–C5, which are 1.359(6) Å and 1.335(6) Å, respectively. The O1–N1–C5–N2–O2 atoms are nearly coplanar as expected due to orbital conjugation. The dihedral angle between nitronyl nitroxide fragment (O1–N1–C5–N2–O2) and the thiophene ring is 10.4°. The intermolecular arrangements in the crystal lattice of **1** are shown in figure 2. Short S $\cdots$ S contacts (3.477 Å) were found among the neighboring molecules of **1**, and a dimer was formed through such intermolecular interactions. The shortest intradimer and interdimer O $\cdots$ O (NITR) distances are 5.494 Å and 4.115 Å, respectively; the latter is expected to play an active role in transmitting the magnetic exchange interactions among these adjacent dimers through space.

3.2. *Crystal structure of (2)*

The crystal structure of **2** is shown in figure 3. The molecule is formed by three copper atoms linked through two μ-1,4 bridging nitroxide ligands and is centrosymmetric.

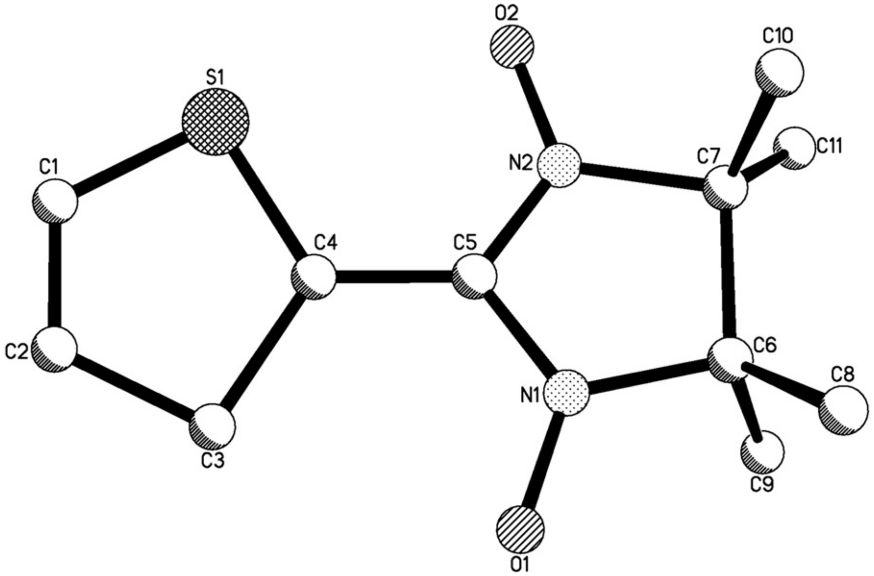

Figure 1. ORTEP drawing of **1**.

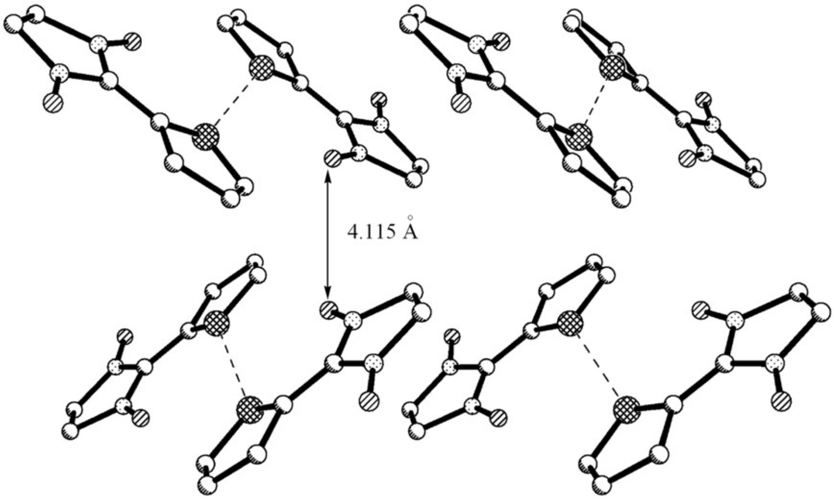

Figure 2. Crystal packing and intermolecular arrangements of **1**.

Two terminal copper atoms Cu2 are pentacoordinate in a distorted square-pyramidal environment to hfac molecules and the oxygen atom of NIT2-thp. The oxygen atom (O2) of nitroxide occupies an equatorial position in the square-pyramid of Cu2, while the axial position is occupied by an oxygen atom (O6) of a hfac molecule. The central copper is hexacoordinate in a distorted octahedral environment, the apical positions are occupied by oxygen (O1) of the two bridging nitroxides, which is confirmed by the bond lengths parameter, and the Cu1–O1 bond length is 2.512(3) Å, much larger than the Cu1–O3 bond length (1.938(3) Å) and the Cu1–O4 bond length (1.931(3) Å).

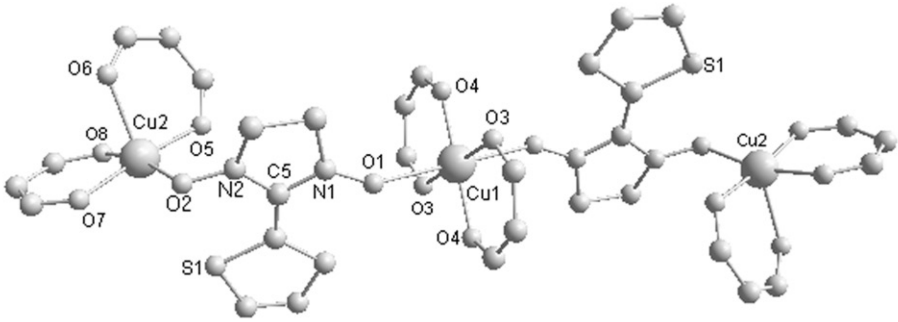

Figure 3. Perspective view of **2**. For clarity, fluorine and hydrogen atoms were omitted.

Three Cu(II) ions are colinear and the distance between Cu1 and Cu2 is 7.8990(9) Å. The N–O bond length of N1–O1 is 1.272(4) Å, shorter than the correlative values observed in **1**, indicating the nitroxide oxygens are only very loosely bonded to the central Cu(II) ion in the apical direction. Meanwhile, the short N–O bond lengths suggest Cu1 is axially elongated, that is to say, the coordination environment of the central Cu1 is an elongated octahedron. The equatorial coordinated N–O bond length of N2–O2 is 1.301(4) Å, implying stronger coordination compared to the apical bonds (N1–O1), but still in the range expected for a coordinated nitroxide [15, 16]. Bond distances and angles in the hfac molecules are in the normal range for this kind of compound [17, 18].

3.3. *Magnetic susceptibility studies of (1) and (2)*

The variable temperature magnetic susceptibilities of **1** were investigated in the 3–300 K region at 10,000 G. The $\chi_M T$ *versus* T and χ_M *versus* T plots are shown in figure 4. The $\chi_M T$ value for **1** at room temperature is 0.72 $cm^3\,mol^{-1}\,K$, slightly lower than expected for two $S_{rad} = 1/2$ uncorrelated spins (0.75 $cm^3\,mol^{-1}\,K$). The values decrease slowly with decreasing temperature, indicating the existence of antiferromagnetic intermolecular interactions between the nitronyl nitroxide radical dimers [19–21].

According to the spin Hamiltonian $\hat{H} = -2J\,\hat{S}_1 \cdot \hat{S}_2$ [22], the magnetic data can be fitted as the following equation:

$$\chi_M = \frac{N_A g^2 \mu_B^2}{3k_B T(3 + e^{-2J/k_B T})}$$

the best fit for the data gives $J = -3.89\,cm^{-1}$, $g = 2$, and the agreement factor R, defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{calcd}]^2/\Sigma[(\chi_M)_{obs}]^2$, is equal to 5.0×10^{-3}. The fitting result is in agreement with the previous analysis. A plausible explanation of the weak magnetic exchange interactions can be rationalized by analyzing the overlap of atomic orbitals belonging to atoms with large spin densities [23]. Indeed, as mentioned above, the intradimer O⋯O (NITR) distance is 5.494 Å, which is too large to be magnetically important, however, the interdimer O⋯O (NITR) distance is short (4.115 Å) and responsible for transmitting the magnetic exchange interactions through space [24–27].

The variable temperature magnetic susceptibilities of **2** were measured in the 3–300 K region at 10,000 G. The plot of $\chi_M T$ *versus* T is shown in figure 5, the $\chi_M T$ value

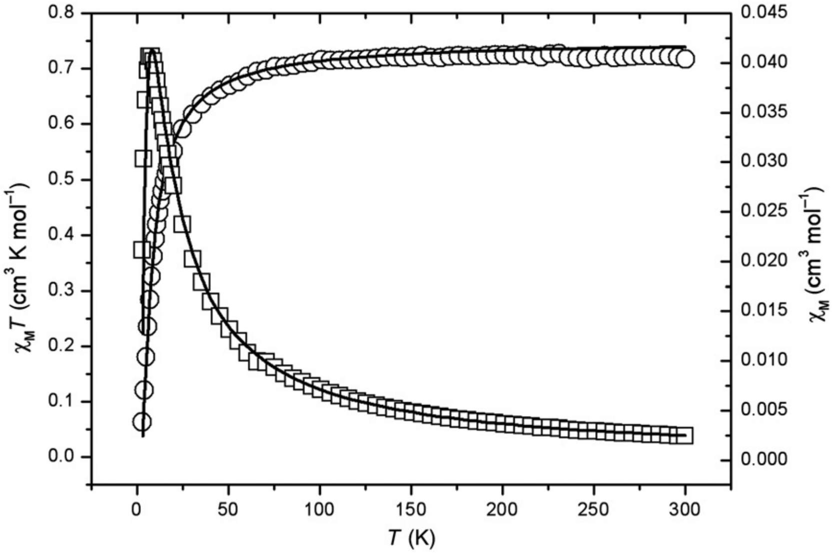

Figure 4. Temperature dependence of $\chi_M T$ (○) and χ_M (□) for **1** and their corresponding theoretical curves (solid lines).

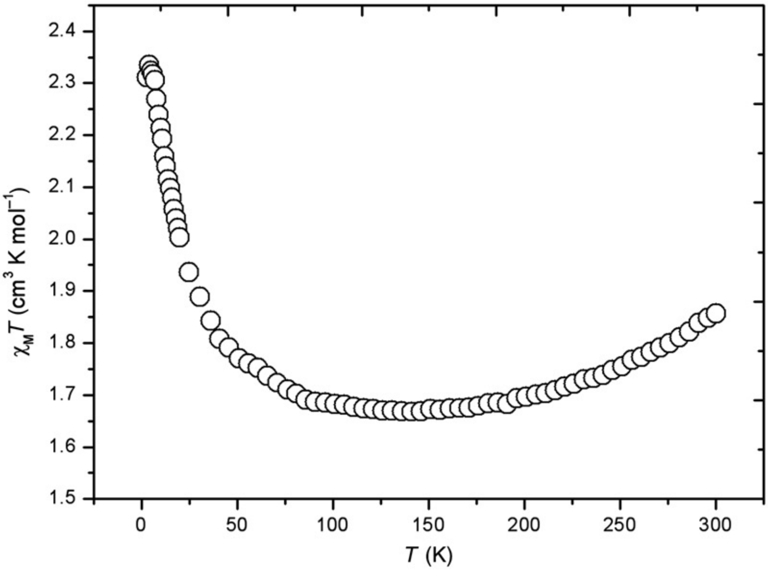

Figure 5. Experimental $\chi_M T$ (○) *vs.* T curve for **2**.

at room temperature is 1.86 cm^3 mol^{-1} K, which compares well with the spin-only value expected for five $S = 1/2$ uncorrelated spins (1.88 cm^3 mol^{-1} K). It has always been found that when a nitroxide is axially bound by its oxygen atom to copper(II), a weak ferromagnetic interaction develops, while when it occupies an equatorial position in the copper(II), the two spins are strongly coupled in an antiferromagnetic way [28, 29]; this also seems in agreement with the result of magnetic data measurement. The magnetic data for **2** could not be fit to a simple five-spin model, even when using only relatively high temperature data. This suggests the presence of significant intermolecular contributions to the observed magnetic behavior, whereas analysis of the crystal packing in the complex does not reveal close intermolecular contacts. In fact, in order to quantitatively evaluate magnetic interactions in the system, all of our attempts to reproduce the susceptibility data through an isotropic Heisenberg form of interaction failed. Clearly the magnetic properties of this complex are unusual and require further studies.

In summary, a new nitronyl nitroxide NIT2-thp (**1**) and its copper(II) complex $[\mathrm{Cu(hfac)_2}]_3\mathrm{(NIT2\text{-}thp)_2}$ (**2**) were obtained and characterized structurally and magnetically. The magnetic analysis revealed that there are weak antiferromagnetic intermolecular interactions between the dimers of **1** and antiferromagnetic interactions and ferromagnetic interactions in **2**.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 623860, and 627630 for structure of these compounds. Copies of the information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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