Inorganica Chimica Acta, *217* (1994) 7–13

A seven-spin cluster formed by an alkyl nitronyl nitroxide biradical and copper(II): crystal structure and magnetic properties

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(Received July 27, 1993)

Abstract

The crystal structure and the magnetic properties of $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$, a novel adduct of $Cu(hfac)_2$ (hfac = hexafluoroacetylacetonate) and the alkyl nitronyl nitroxide biradical NITnPr(3-NIT) = 1,3-bis(1′-oxyl-3′-oxide-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazol-2′-yl)propane, are reported. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.740(3)$, $b = 14.316(3)$, $c = 14.737(2)$ Å, $\alpha = 106.5(1)$, $\beta = 103.3(1)$, $\gamma = 111.5(2)°$ and $Z = 2$. In the complex one copper(II) ion is hexacoordinated, with two NO donor groups of two biradicals in the axial positions, while the other two copper(II) ions have a square-pyramidal geometry, with an NO group in the apical position. A cluster of seven spins magnetically interacting is the result. The magnetic susceptibility measurements in the temperature range 3–280 K show an increase of the $\chi_m T$ product on lowering the temperature, followed by a decrease for temperatures lower than 8.0 K. The susceptibility data have been interpreted with the help of magneto-structural correlations. They are consistent with strong antiferromagnetic couplings ($J'' > 500$ cm^{-1}) between the square-pyramidal copper(II) and the coordinating radical spins, and two ferromagnetic couplings ($J \approx -37$ cm^{-1}) between the hexacoordinated copper(II) and the two spins of the coordinating radicals.

Key words: Crystal structures; Magnetism; Copper complexes; Nitronyl complexes; Nitroxide complexes; Radical complexes

Introduction

The increasing interest in the study of magnetic molecular materials [1] demands the development of novel synthetic strategies. The approach in which organic radicals are coupled to metal ions [2] has already provided many magnetically ordered materials, like $V(TCNE)_2$, which behaves as a disordered ferromagnet at room temperature [3]; $[M(Me_5Cp)]_2R$, where $M = Fe^{II}$, Mn^{II}, and R = TCNE, TCNQ, with a maximum ordering temperature of 8.8 K [4–6]; $(cat)_2Mn_2[Cu(opba)]_3(DMSO)_2 \cdot 2H_2O$, where cat^+ is the nitronyl nitroxide radical cation 2-(4-*N*-methyl-pyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide, which orders below 22.5 K [7]. We synthesized compounds of formula $M(hfac)_2NITR$, where $M = Mn^{II}$, Ni^{II}, hfac = hexafluoroacetylacetonate and NITR is the nitronyl nitroxide radical 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide [8, 9]; $M(hfac)_3NITR$, with M = Dy, Er [10] and $[Mn(F_5bz)_2]NITR$, with R = Me, Et, and F_5bz = pentafluorobenzoate [11], which have a maximum critical temperature of 25 K.

In order to synthesize compounds with higher critical temperatures we are currently trying to vary both the radicals and the co-ligands. A logical evolution of this approach seems to be the use of nitronyl nitroxide biradicals as ligands towards metal ions. Several stable nitronyl nitroxide biradicals [12, 13] and polyradicals [14] were synthesized years ago, but for a long time they have been neither the object of investigation in the solid state nor used as ligands. Recently the magnetic properties of the two aryl bis-nitronyl nitroxides **I** and **II** were investigated [15, 16], and their complexes with Cu^{II} were reported [16]. An antiferromagnetic exchange interaction between the two spins in the biradicals was

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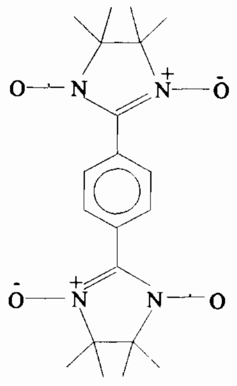
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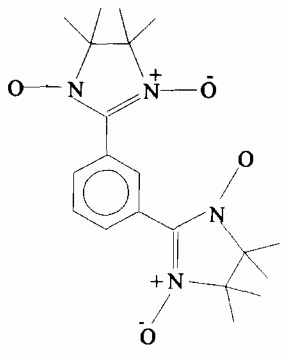
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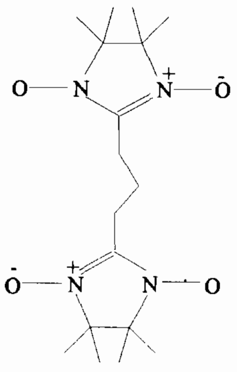
III

found for **I**, while in **II** it is not clearly established whether the interaction is either negligible or ferromagnetic. In the copper complexes the biradicals **I** and **II** were found to use all their NO groups as donors towards copper(II) ions to yield either polynuclear or extended structures.

The alkyl bis-nitronyl nitroxide **III** (NITnPr(3-NIT) = 1,3-bis(1′-oxyl-3′-oxide-4′,4′,5′,5′-tetramethyl-4,5-dihydro-1*H*-imidazol-2′-yl)propane) is now the object of our interest. Although the presence of the $-(CH_2)_3-$ skeleton, instead of the benzene ring as in **I** and **II**, is not expected to transfer in an efficient way the exchange interactions between the two spins of the biradical, the flexibility of the skeleton might in principle lead to interesting structures when NITnPr(3-NIT) acts as a ligand towards metal ions. We present here the crystal structure and the magnetic properties of $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$ a polynuclear complex of the biradical and $Cu(hfac)_2$.

Experimental

Synthesis

$Cu(hfac)_2$ was prepared by reported procedures [17]. NITnPr(3-NIT) was prepared according to the Ullman procedure [12] using glutaric aldehyde to condensate 2,3-dihydroxylamino-2,3-dimethylbutane and liquid–solid chromatography (acetone/CH_2Cl_2 on Al_2O_3 Act. III) to separate NITnPr(3-NIT) from the monocondensate radical and from their iminonitroxide derivatives. A 180 mg sample of anhydrous $Cu(hfac)_2$ and 66 mg of NITnPr(3-NIT) were dissolved in warm n-hexane, then the solution was filtered and allowed to cool down to room temperature. After a few days liver red crystals formed, which analyzed satisfactorily for $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$. *Anal.* Calc. for $Cu_3C_{64}F_{36}H_{66}N_8O_{20}$: C, 35.88; H, 3.08; N, 5.23. Found: C, 35.86; H, 3.13; N, 5.18%.

Crystal data

A well shaped crystal of $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$ of *c.* $0.2\times0.2\times0.4$ mm size was used for the X-ray data collection. The diffraction experiment was carried out at room temperature on an Enraf-Nonius CAD 4 automatic diffractometer with the ω–2θ scan technique in the range 2.5–25.5°. Mo Kα radiation was used. During the measurements the crystal decay was tested by detecting the intensity of standard reference reflections at intervals of 6 h. Unit cell parameters were derived from a least-squares fit to the setting angles of 25 intense reflections in the 9.7–14.2° θ range.

All data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the Ψ scan, was applied [18] (max., min. transmission factor = 0.99, 0.94). The refinement was made with 4489 reflections with $I > 3.0\sigma(I)$. Unit cell parameters and other experimental parameters are reported in Table 1.

The structure was solved by direct methods, which afforded the positions of the metal atoms; all the remaining non-hydrogen atoms were located by subsequent difference-Fourier syntheses. Anomalously large thermal parameters and residual peaks in difference Fourier maps showed evidence of statistical disorder, as a result of two alternative orientations for the fluorine atoms of four of six CF_3 groups. Least-squares refinement of their occupancy factors led, for the majority of sites, to the values of 0.70(1), which in the final stage of refinement, were held fixed. The refinement was carried out by least-squares calculations (in two blocks) including the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms. The hydrogen atoms were treated as fixed contributors in calculated positions, assuming a temperature factor 1 Å^2 greater than that of the attached carbon atoms. The highest residual was 0.7 e/Å^3. This model converged to $R = 0.074$ and $R_w = 0.077$, $w = 0.9/[\sigma^2(F) + 0.001F_o^2]$.

TABLE 1. X-ray data for $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$

Crystal parameters (293 K)	
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	11.740(3)
b (Å)	14.316(3)
c (Å)	14.737(2)
α (°)	106.5(1)
β (°)	103.3(1)
γ (°)	111.5(2)
V (Å^3)	2225.1(18.6)
Z	2
Molecular formula	$Cu_3C_{64}H_{66}N_8O_{20}F_{36}$
Molecular weight	2141.85
ρ_{calc} (g/cm^3)	1.60(1)
ρ_{obs} (g/cm^3) (by flotation)	1.61(1)
$F(000)$	1077
μ(Mo Kα) (cm^{-1})	6.5
Data collection	
Radiation, λ (Å)	graphite monochromated Mo Kα, 0.71069
Reflections collected	$-14\leqslant h\leqslant 14$; $-17\leqslant k\leqslant 17$; $0\leqslant l\leqslant 17$
Scan type	ω–2θ
θ Range (°)	2.5–25.5
Crystal size (mm)	0.2×0.2×0.4
No. standard reflections	2 every 6 h (no significant changes)
No. unique reflections	5473 (R merging = 0.016)
No. observed reflections	4489 with $I>3\sigma(I)$
Max./min. transmission	0.99/0.94
No. parameters (last cycle)	477 (9.4 observations per parameter)
R	0.074
R_w	0.077

Complex neutral-atom scattering factors [19] were employed throughout; major calculations were carried out on a VAX 6210 computer, using the SHELX 76 program package [20] and the ORTEP [21] plotting program.

Final fractional coordinates are given in Table 2.

Magnetic and EPR measurements

The magnetic susceptibility of a powdered sample was measured in the temperature range 2.9–270 K in a field of 2 T using a Métronique Ingéniérie MS03 SQUID magnetometer. The diamagnetic contribution to the magnetic susceptibilities, which was estimated from Pascal's constants, was found to be very large and important in the high temperature range: at room temperature it was about 30% of the total susceptibility.

EPR spectra of a powdered sample were obtained with a Varian E9 spectrometer at X-band frequency; low temperature spectra were recorded using an Oxford Instruments ESR9 liquid-helium continuous-flow cryostat.

TABLE 2. Final fractional coordinates for $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$

Atom	x/a	y/b	z/c
Cu(1)	0.0	0.0	0.0
Cu(2)	0.24350(9)	−0.53369(8)	0.36401(8)
O(1)	0.0584(5)	−0.0405(4)	0.1194(4)
O(2)	0.1494(5)	0.0437(5)	−0.0734(4)
C(1)	0.2374(8)	0.0371(7)	−0.0330(8)
C(2)	0.2456(8)	0.0078(8)	0.0599(8)
C(3)	0.1579(9)	−0.0308(7)	0.1305(8)
C(4)	0.180(1)	−0.070(1)	0.228(1)
C(5)	0.3487(9)	0.066(1)	−0.113(1)
F(1)	0.078(1)	−0.053(1)	0.297(1)
F(2)	0.218(1)	−0.1688(7)	0.247(1)
F(3)	0.258(1)	−0.028(1)	0.252(1)
F(1′)	0.274(3)	−0.136(4)	0.235(2)
F(2′)	0.101(4)	−0.097(3)	0.295(3)
F(3′)	0.194(4)	−0.009(3)	0.257(3)
F(4)	0.403(1)	0.114(2)	−0.075(1)
F(5)	0.427(1)	−0.021(1)	−0.129(1)
F(6)	0.320(1)	0.1257(9)	−0.190(1)
F(4′)	0.371(4)	0.134(4)	−0.091(4)
F(5′)	0.439(3)	0.008(3)	−0.109(4)
F(6′)	0.342(3)	0.091(3)	−0.198(3)
F(7)	0.020(1)	−0.264(1)	0.475(1)
F(8)	0.150(1)	−0.227(1)	0.526(1)
F(9)	0.079(2)	−0.349(1)	0.613(1)
F(7′)	0.018(3)	−0.313(3)	0.528(3)
F(8′)	0.120(4)	−0.225(3)	0.494(3)
F(9′)	0.103(4)	−0.326(3)	0.605(3)
O(7)	0.1759(5)	−0.4549(5)	0.4645(4)
O(8)	0.4214(5)	−0.4973(5)	0.3495(5)
O(9)	0.2440(5)	−0.6059(4)	0.2703(4)
O(10)	0.2720(6)	−0.6573(5)	0 4597(5)
C(23)	0.4171(8)	−0.4190(8)	0.3734(8)
C(24)	0.3221(9)	−0.3567(8)	0.4256(7)
C(25)	0.2100(9)	−0.3789(7)	0 4665(6)
C(26)	0.116(1)	−0.3079(9)	0.5215(9)
C(27)	0.541(1)	−0.384(1)	0.330(1)
C(28)	0.2895(8)	−0.7431(7)	0.4454(8)
C(29)	0.2901(8)	−0.7704(7)	0.3607(8)
C(30)	0.2672(7)	−0.6993(7)	0.2812(7)
C(31)	0.311(1)	−0.8218(9)	0.530(1)
C(32)	0.2615(9)	−0.7341(9)	0.1937(9)
F(10)	0.3729(8)	0.4549(9)	0.6338(9)
F(11)	0.4212(9)	0.3830(9)	0.7590(8)
F(12)	0.4630(8)	0.3061(9)	0.652(1)
F(13)	0.6532(6)	0.8159(5)	0.8229(5)
F(14)	0.8443(6)	0.7587(6)	0.7893(6)
F(15)	0.2683(6)	0.3332(5)	0.1133(5)
F(16)	0.419(2)	−0.876(2)	0.524(2)
F(17)	0.263(3)	−0.895(2)	0.547(2)
F(18)	0.276(2)	−0.801(1)	0.6160(9)
F(16′)	0.359(4)	−0.895(4)	0.515(3)
F(17′)	0.241(5)	−0.846(4)	0.577(4)
F(18′)	0.386(5)	−0.815(2)	0.567(2)
O(3)	0.1016(5)	−0.1630(4)	−0.0350(4)
O(4)	0.4947(5)	−0.3267(5)	−0.1546(5)
O(5)	0.1198(6)	−0 4175(5)	−0.0098(4)
O(6)	0.2071(5)	−0.4101(4)	0.2722(4)
C(6)	0.3071(7)	−0.2470(6)	−0.0726(6)
C(7)	0.2018(7)	−0.1878(7)	−0.1995(6)

(*continued*)

TABLE 2. (*continued*)

Atom	x/a	y/b	z/c
C(8)	0.3201(7)	−0.2676(7)	−0.2302(6)
C(9)	0.2073(9)	−0.0812(7)	−0.2485(7)
C(10)	0.0823(8)	−0.2077(8)	−0.2089(8)
C(11)	0.3984(8)	−0.2363(8)	−0.3269(7)
C(12)	0.3024(8)	−0.3722(7)	−0.2229(7)
C(13)	0.3353(8)	−0.2572(7)	0.0212(7)
C(14)	0.3939(7)	−0.3618(7)	0.0677(7)
C(15)	0.3270(7)	−0.4437(7)	0.0742(7)
C(16)	0.1944(7)	−0.4189(6)	0.1213(6)
C(17)	0.0075(7)	−0.3661(6)	0.2282(6)
C(18)	−0.0180(7)	−0.3988(6)	0.1445(6)
C(19)	−0.0474(8)	−0.4149(7)	0.3286(6)
C(20)	−0.0169(8)	−0.2530(7)	0.2153(7)
C(21)	−0.0422(8)	−0.5039(7)	0.1732(7)
C(22)	−0.1139(8)	−0.3229(8)	0.0923(8)
N(1)	0.1969(6)	−0.1991(5)	−0.0953(5)
N(2)	0.3827(6)	−0.2785(5)	−0.1502(5)
N(3)	0.1054(6)	−0.4937(5)	0.0749(5)
N(4)	0.1465(6)	−0.4035(5)	0.2076(5)

Results and discussion

Crystal structure

The structural unit, which consists of a trinuclear complex, [Cu(hfac)$_2$]$_3$[NITnPr(3-NIT)]$_2$, is depicted in Fig. 1. Three copper atoms are bridged by two NITnPr(3-NIT) biradicals. The central copper, Cu(1), which sits at the inversion centre, is hexacoordinated by two pairs of hfac oxygens, defining four in-plane coordination sites, and two oxygens of two NITnPr(3-NIT) which occupy the apical coordination sites. The terminal copper atom, Cu(2), has a distorted square-pyramidal coordination, three oxygens of two hfac molecules defining the in-plane coordination sites, the oxygen of an NITnPr(3-NIT) molecule occupying the remaining basal site, and the fourth oxygen of an hfac occupying the apical coordination site. The square-planar coordination polyhedron of Cu(2) is substantially flat with small deviations from the average planes (±0.17 Å), Cu(2) lying 0.21 Å above the coordination plane. The dihedral angle between the two hfac ring planes of Cu(2) is 100.6°. The Cu(1)–Cu(2) distance is 8.289(5) Å.

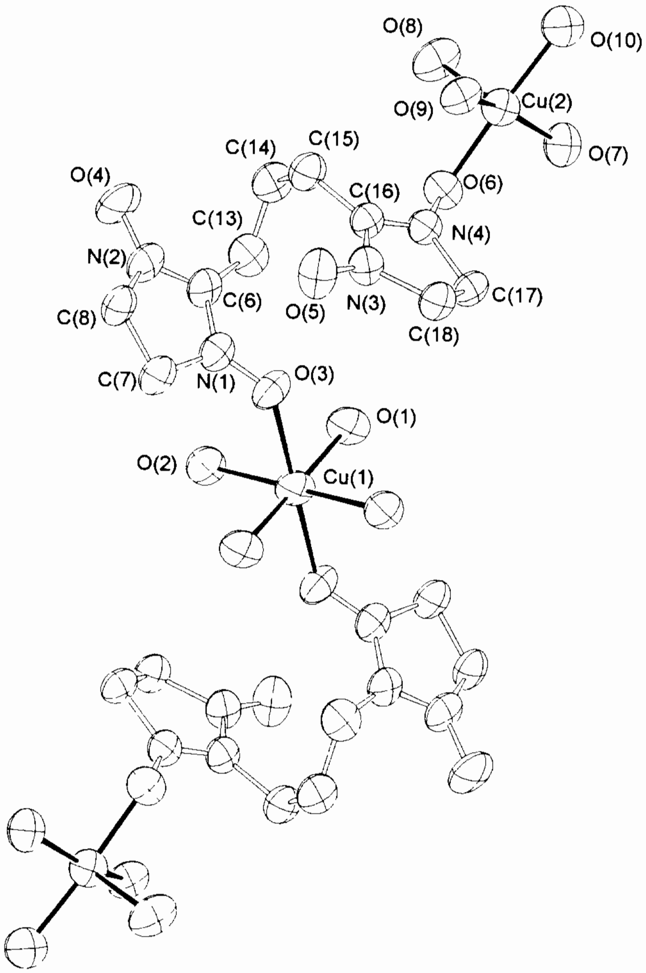

Fig. 1. ORTEP view of [Cu(hfac)$_2$]$_3$[NITnPr(3-NIT)]$_2$. Carbon and fluorine atoms of the hfac and methyl groups have been omitted for the sake of clarity.

The two radical fragments within the NITnPr(3-NIT) molecules have quite different interatomic distances. The fragment bound to Cu(1) is almost symmetrical, with the two N–O bonds of approximately the same length (N(1)–O(3) 1.287(6), N(2)–O(4) 1.272 Å), as well as the two C–N bonds (N(1)–C(6) 1.341(9), N(2)–C(6) 1.335(9) Å). On the contrary, the radical bound to Cu(2) is very asymmetric: the N(4)–O(6) bond, corresponding to the donor oxygen, is much longer than the N(3)–O(5) bond (N(4)–O(6) 1.307(9), N(3)–O(5) 1.248(8) Å), while the N(4)–C(16) bond is much shorter than the N(3)–C(16) bond (N(4)–C(16) 1.31(1), N(3)–C(16) 1.34(1) Å). A similar bond length alternation was found in the other copper(II)–nitronyl nitroxide complexes in which the radical is bound to copper(II) in the equatorial position [22]. Planarity has been found in the two nitronyl nitroxide fragments O(3)–N(1)–C(6)–N(2)–O(4) and O(6)–N(4)–C(16)–N(3)–O(5) with deviation from the average planes in the range −0.22/+0.23 and −0.02/+0.01 Å, respectively. The two average planes are almost parallel to each other, forming an angle of 19.36°, and short interatomic distances between atoms of the two fragments were found: N(1)–O(5), 3.335; N(3)–O(3), 3.454; O(5)–O(3), 3.509; N(1)–N(3), 3.589 Å. These short interatomic distances between the NO groups in the two moieties of NITnPr(3-NIT) are related to the bent conformation taken on by the C(6)–C(13)–C(14)–C(15)–C(16) skeleton which bridges the two nitronyl nitroxide fragments. The main intermolecular contacts involving the $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$ trinuclear complexes related by translations are through the NO groups. The shortest contact distance is 4.089 Å, between O(5) and O(5″) (O(5″): $-x, -1-y, -z$). Another meaningful contact is O(4)–Cu(2‴) = 4.171 Å (Cu(2‴): $1-x, -1-y, -z$), with the NO group interacting with the square-pyramidal copper atom. Selected bond distances and angles are reported in Table 3.

TABLE 3. Selected bond distances and angles for $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$

O(1)–Cu(1)	1.945(6)	O(2)–Cu(1)	1.952(5)
O(3)–Cu(1)	2.415(5)	O(7)–Cu(2)	1.961(5)
O(8)–Cu(2)	2.221(6)	O(9)–Cu(2)	1.928(6)
O(10)–Cu(2)	1.959(5)	O(6)–Cu(2)	1.938(4)
O(2)–Cu(1)–O(1)	91.3(2)	O(3)–Cu(1)–O(1)	89.3(2)
O(3)–Cu(1)–O(2)	88.0(2)	O(8)–Cu(2)–O(7)	87.0(2)
O(9)–Cu(2)–O(7)	157.4(2)	O(9)–Cu(2)–O(8)	115.0(2)
O(10)–Cu(2)–O(7)	91.6(2)	O(10)–Cu(2)–O(8)	96.1(2)
O(10)–Cu(2)–O(9)	91.3(2)	O(6)–Cu(2)–O(7)	86.9(2)
O(6)–Cu(2)–O(8)	85.8(2)	O(6)–Cu(2)–O(9)	89.3(2)
O(6)–Cu(2)–O(10)	177.5(2)	O(3)–O(1)–Cu(1)	125.8(5)
C(1)–O(2)–Cu(1)	124.7(5)	C(23)–O(8)–Cu(2)	118.7(5)
C(30)–O(9)–Cu(2)	126.7(5)	C(28)–O(10)–Cu(2)	124.8(5)

Magnetic data

The magnetic susceptibility data, reported in $\chi_m T$ versus T per molecular unit $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$, are shown in Fig. 2. The room temperature value, $\chi_m T \cong 1.1$ emu K mol^{-1}, is much lower than expected for the seven $S = 1/2$ spins of the molecular unit in the high temperature limit of uncorrelated spins ($\chi_m T \cong 2.625$ emu K mol^{-1}), indicating the presence of antiferromagnetic coupling. $\chi_m T$ increases on decreasing the temperature and passes through a maximum at $T \approx 8$ K ($\chi_m T \cong 1.73$ emu K mol^{-1}). The polycrystalline powder EPR spectra show a broad feature at $g = 2.13$, and a sharper signal at $g \approx 2$. On cooling to liquid helium temperature the signal at $g \approx 2$ is better resolved giving $g_\parallel = 2.0$ and $g_\perp = 2.3$. These values are typical of a trigonal bipyramidal copper(II) complex [23] and are presumably due to an impurity.

In the interpretation of the magnetic behaviour of $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$ we have to consider the exchange interactions between the seven $S = 1/2$ spins. The spin system can be described through a seven spin linear cluster, as sketched below

$$\begin{array}{ccccccc} \text{Cu2} & \text{R2} & \text{R1} & \text{Cu1} & \text{R1'} & \text{R2'} & \text{Cu2'} \\ \mathbf{6} & \text{---}\mathbf{4} & \text{---}\mathbf{2} & \text{---}\mathbf{1} & \text{---}\mathbf{3} & \text{---}\mathbf{5} & \text{---}\mathbf{7} \\ J'' & J' & J & J & J' & J'' & \end{array}$$

with a corresponding Heisenberg exchange Hamiltonian

$$\mathscr{H} = J(S_1S_2 + S_1S_3) + J'(S_2S_4 + S_3S_5) + J''(S_4S_6 + S_5S_7) \quad (1)$$

J and J'' represent the coupling constants of the interactions between Cu(1) and Cu(2), respectively, and the nitronyl nitroxide biradicals spins, while J' refers to the coupling between the spins of the same biradical molecule.

Concerning the exchange interactions between the Cu(II) ions and the nitronyl nitroxides, magneto-structural correlations are well described [22]. In particular, when the nitronyl nitroxide is bound to an octahedral

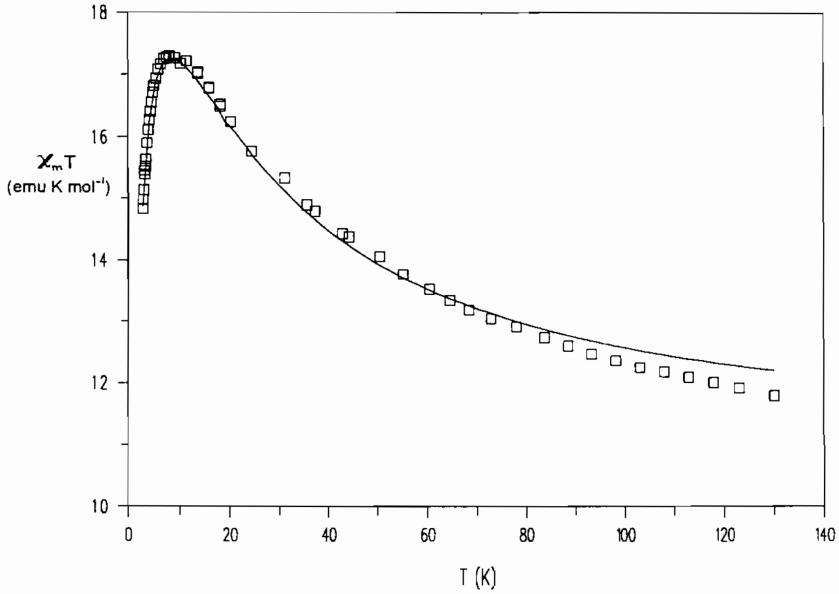

Fig. 2. Temperature dependence of $\chi_m T$ for the molecular unit $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$. The solid line represents the best fit calculated values.

Cu(II) ion in the axial position, as in the case of the Cu(1) ion, the coupling is expected to be ferromagnetic. On the contrary, an extremely strong antiferromagnetic coupling, with a constant larger than 500 cm^{-1} [24, 25] has been found in the case of nitronyl nitroxide coordinating a square-pyramidal Cu(II) ion in the basal position, as it occurs here for the Cu(2) ions. Therefore, assuming that the two spins of the symmetry related Cu(2) ions are completely coupled to the spins of the nitronyl nitroxides to which they are bound to give diamagnetic states, we can drop the last two terms of the Hamiltonian (1) and describe the cluster through the simplified spin Hamiltonian

$$\mathscr{H} = J(S_1S_2 + S_1S_3) \qquad (2)$$

This assumption is qualitatively in good agreement with the room temperature value of $\chi_m T$ which is that expected for three uncorrelated $S = 1/2$ spins ($\chi_m T = 1.125$ emu K mol^{-1}, with $g = 2$). The rise of $\chi_m T$ on decreasing temperature agrees with the expected ferromagnetic coupling between the Cu1 spin and the two nitronyl nitroxide moieties bound to it. This coupling would eventually lead to an $S = 3/2$ ground state, which requires a $\chi_m T$ value of about 1.875 emu K mol^{-1}. This value is not experimentally reached, due to the decrease of $\chi_m T$ in the low temperature range. Such a decrease cannot be attributed to intermolecular magnetic interactions, since each three-spin system is magnetically well isolated from the others; however saturation effects, no more negligible at low temperature, are expected to cause a decrease in $\chi_m T$. The fitting of the $\chi_m T$ versus T curve has been performed by using the Hamiltonian (2) and introducing the effect of the magnetic field as a perturbation to the energy levels of the coupled system. The least-squares procedure yields $J = -37.3$ cm^{-1}, with $g = 1.96$ and $R = 2.46 \times 10^{-3}$*. The result of the fitting is shown in Fig. 2. The small g value may be due to the uncertainties associated with the high temperature values determined by the low magnetic susceptibilities and the large Pascal's correction. The value obtained from the fitting for the coupling constant J is in the range of values (-20 to -65 cm^{-1}) found in other copper(II)–nitronyl nitroxide complexes with the radical in the axial position.

Conclusions

Although the final goal of reaching an extended structure of interacting spins by using $Cu(hfac)_2$ and the nitronyl nitroxide biradical NITnPr(3-NIT) failed, some interesting considerations arise from the analysis of the crystal structure and the magnetic properties of the complex $[Cu(hfac)_2]_3[NITnPr(3\text{-}NIT)]_2$. First of all we note that only two NO groups of NITnPr(3-NIT) are used to coordinate to copper(II) ions and to give relevant exchange interactions with them; the peripherical Cu(2) ions, which are pentacoordinated, do not allow these extended structures to be obtained. However we think that the substitution of copper(II) with manganese(II), which prefers the hexacoordination, could allow all four NO groups to bind to the metal ions, and favour an extended structure of interacting spins. The flexibility of the skeleton in this biradical is thought to play an important role, in order to avoid steric hindrance problems in the crystal packing. We are working in this direction.

Supplementary material

Tables 1S–3S listing anisotropic thermal parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogens, and bond lengths and angles are available from the authors on request.

Acknowledgements

MURST and 'Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate' are gratefully acknowledged for grants, and the 'Centro Interdipartimentale di Calcolo Automatico et Informatica Applicata' for computer facilities.

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*$R = [\Sigma(\chi_{obs}T - \chi_{calc}T)^2 / \Sigma(\chi_{obs}T)^2]^{1/2}$.

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