Article

Synthesis, Structural and Magnetic Characterization of a New Copper(II)-Nitronyl Nitroxide Radical Complex

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Neste trabalho é descrito o estudo das propriedades magnéticas de um novo complexo cobre(II)-NIT, onde NIT representa um radical do tipo nitronil nitróxido. O precursor $(NBu_4)_4[Cu_2(bopba)]$ (onde NBu_4^+ é o cátion tetrabutilamônio e bopba é o bis-*o*-fenilenobis(oxamato)) teve a sua estrutura cristalina determinada por difração de raios X e também foi caracterizado magneticamente. Através da complexação deste precursor com o radical catiônico nitronil nitróxido, um novo complexo foi obtido, o $(pEtRad)_4[Cu_2(bopba)]$ (onde pEtRad$^+$ é o radical catiônico *para*-2-(4-piridil)-4,4,5,5-tetrametilimidazolina-1-oxil-3-óxido). Os estudos magnéticos sugerem que neste complexo existe uma competição entre interações ferromagnéticas e antiferromagnéticas. A interação ferromagnética pode ser explicada com base na ortogonalidade dos orbitais magnéticos envolvidos.

In this work we describe the structure and the magnetic properties of a new copper(II)-NIT complex, where NIT stands for nitronyl nitroxide radical. This was achieved using $(NBu_4)_4[Cu_2(bopba)]$ as a precursor (where NBu_4^+ is the tetrabutylammonium cation and bopba is bis-*o*-phenylenebis(oxamate)), whose crystal structure was resolved and its magnetics properties studied. From the reaction of this precursor with a cationic nitronyl nitroxide radical, a new compound was prepared and magnetically characterized, namely $(pEtRad)_4[Cu_2(bopba)]$ (where pEtRad$^+$ stands for the cationic *para*-2-(4-pyridil)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide radical). The magnetic properties suggest that in this six-spin complex there is a competition between short range ferromagnetic and antiferromagnetic interactions. The ferromagnetic interaction can be explained by the orthogonality of the involved magnetic orbitals.

Keywords: molecular magnetism, coordination complexes, nitronyl nitroxide radical

Introduction

The synthesis of molecule-based magnetic materials has been the object of increasing interest in the last years. In fact, the molecular nature of these compounds allows one to obtain magnetic properties[1] in association with chemical and optical properties. These molecule-based magnets are potential building-blocks for molecular electronic devices and can eventually be exploited in the so-called molecular electronics.[2]

In order to obtain magnetic molecular materials,[3] several approaches are followed, namely: metal-metal, purely organic, or metal-radical approach, depending on the chemical nature of the magnetic centers. The most usual building-blocks used to prepare metal-metal molecular magnets are probably the hexacyano-

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metalates[4] $[M(CN)_6]^{3-}$ and the trisoxalatometalates[5] $[M(C_2O_2)_3]^{3-}$ (where M is a transition metal ion). Due to their capacity to establish bonds in three directions, these building-blocks may lead to three-dimensional magnetic networks. In the case of the purely organic approach, nitronyl nitroxide radicals (NIT) were intensively investigated[6] after the discovery of the first purely organic ferromagnet 2-(*p*-nitrophenyl)nitronyl nitroxide, in 1991.[7] The NIT radicals are also used in the metal-radical approach,[8] where they are combined with different paramagnetic metal ions to prepare a large number of coordination complexes. With the $M(hfac)_2$ (hfac = hexafluoroacetylacetonate) para-magnetic unit, one-dimensional ferrimagnetic chains were obtained, leading to long range ordering around 10 K.[9] The most famous example of these chains is the $Co(hfac)_2(NITPhOMe)$ (where NITPhOMe is 4'-methoxyphenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) which was reported to behave as a molecular magnetic nanowire.[10] Within the metal-radical approach there are two goals. One is the rational design of molecular compounds exhibiting spontaneous magnetization. The other is the study of the relation between the structure and the magnetic properties of this kind of compounds.[11]

In this paper we present the structure and magnetic properties of a dimeric copper(II) building-block $[Cu_2(bopba)]^{4-}$ (where bopba stands for bis-*o*-phenyl-enebis(oxamate)) and the synthesis and characterization of a new $[Cu_2(bopba)]^{4-}$-NIT compound. The nitronyl nitroxide radical chosen was the cationic *para*-2-(4-pyridil)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, also named pEtRad[+]. A schematic representation of these two magnetic blocks is given in Figure 1.
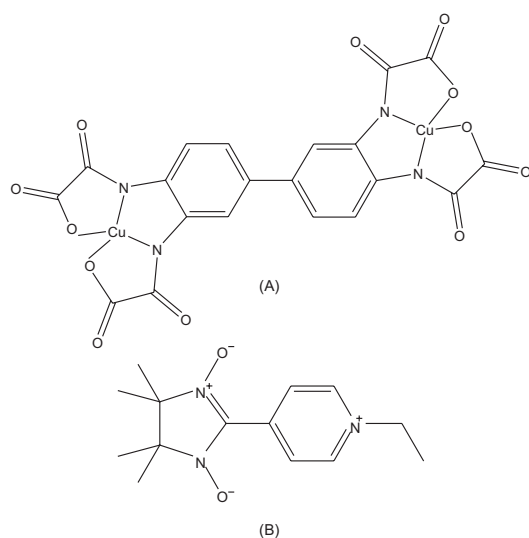

Figure 1. Schematic representation of the (A) $[Cu_2(bopba)]^{4-}$ and (B) pEtRad[+] magnetic blocks.

Experimental

Reagents

All chemicals were purchased from Fluka and Aldrich and used without further purification.

Spectroscopic measurements

Infrared spectra were measured over the region 400-4000 cm^{-1} with a Nicolet Magna 760 FT-IR instrument, with 4 cm^{-1} resolution. The samples were examined as KBr pellets.

Elemental analysis

Carbon, nitrogen and hydrogen contents were determined on a Perkin–Elmer 2400 apparatus.

Synthesis of the $(NBu_4)_4[Cu_2(bopba)]$ (1) and the nitronyl nitroxide radical precursors

The tetraethyl ester bis-*o*-phenylenebis(oxamate) (H_4Et_4bopba) was synthesized following the synthetic method used to prepare H_2Et_2opba[12] (where H_2Et_2opba is *ortho*-phenylenebis(oxamate)), with an increase of two hours in the reaction time. The product is a white polycrystalline powder (yield = 83%).

The $(NBu_4)_4[Cu_2(bopba)]$ (1) complex was synthesized as described previously.[10,13] Tiny crystals were obtained by slow evaporation of a solution containing $(NBu_4)_4[Cu_2(bopba)]$ and acetonitrile at room temperature. Single crystals obtained by this procedure are brown-red and exhibit prismatic elongated habit. All attempts to obtain larger crystals have failed.

The ethyl-pyridyl substituted nitronyl nitroxide radical was prepared and purified according to the method described in the literature.[14,15]

Synthesis of the $(pEtRad)_4[Cu_2(bopba)] \cdot 2(CH_2Cl_2)$ (2)

Dichloromethane solutions of $(NBu_4)_4[Cu_2(bopba)]$ and (pEtRad)I were mixed at room temperature. After 30 minutes under stirring, the brown microcrystalline powder obtained was filtered and washed with methanol and dichloromethane.

Anal. found: C, 50.40; H, 5.04; N, 12.21.; Cu, 6.77; Calc. for $C_{78}H_{94}Cl_4Cu_2N_{16}O_{20}$: C, 50.78; H, 5.13; N, 12.14.; Cu, 6.89. IR spectroscopy: 1620-1640 cm^{-1}: ν(C=O); 2850-3000 cm^{-1}: ν(C-H); 3500 cm^{-1}: ν(OH).

Magnetic measurements

Variable-temperature magnetic susceptibility and isothermal magnetization measurements were performed on polycrystalline samples in the temperature range 2.5-300 K and in the field range 0-60 kOe with a Cryogenics S-600 SQUID magnetometer.

Crystallography

X-ray diffraction data collection on a $(NBu_4)_4$ $[Cu_2(bopba)]$ single crystal was performed on the Xcalibur CCD Diffractometer from the Swiss Norwegian Beam Line of the European Synchrotron Radiation Facility (SNBL-ESRF) at 120 K using radiation with $\lambda = 0.80$ Å. The sample was cooled with a nitrogen gas stream controlled by an Oxford Cryosystem apparatus.[16] The Crysalis suite[17] was employed to integrate the intensities. Scaling based on the minimization of the R_{int} parameter was applied to correct the data due to the incoming beam intensity decay. No absorption correction was applied to the data set.

The $(NBu_4)_4[Cu_2(bopba)]$ crystal used in this experiment was quite small, about $0.5 \times 0.1 \times 0.5$ mm^3. It was also quite bad X-ray scatterer and the best $I/\sigma(I)$ ratio verified at 0.85-0.80 Å of resolution shell was 2.3. All together, these factors limited the final data quality and consequently the refinement statistics.

Results and Discussion

Description of the structure of the $(NBu_4)_4[Cu_2(bopba)]$ complex

The $(NBu_4)_4[Cu_2(bopba)]$ structure was solved by direct methods in the non-centrosymmetric space group $P2_1$ using the SHELXS program.[18] The positions of all atoms of the $[Cu_2(bopba)]^{4-}$ molecule could be unambiguously assigned on consecutive difference Fourier maps; however, the positions of some carbon atoms of the NBu_4^+ molecules were not easily identified due to structural disorder. Refinements were performed using SHELXL[17] based on F^2 through full-matrix least square routine. Restraints have been used to fix the phenyl geometry in the $[Cu_2(bopba)]^{4-}$ moiety. Split positions were assigned to several carbons of the NBu_4^+ groups and their geometry, isotropic ADPs and occupation parameters were restrained and refined accordingly. Hydrogen atoms were added to the structure according to the riding model.[19] All disordered atoms had their ADPs refined anisotropically. Despite the disorder, the final model gives acceptable results. Sample characteristics, data collection, data reduction and refinement parameters are summarized in Table 1; selected atomic parameters are listed in Table 2.

The structure of the copper(II) building block is shown in Figure 2. For the sake of simplicity, the NBu_4^+ cations

Table 1. Crystal data and structure refinement for $(NBu_4)_4[Cu_2(bopba)]$

Empirical formula	$C_{84} H_{150} Cu_2 N_8 O_{12}$
Formula weight/(g mol^{-1})	1591.20
Crystal system	Monoclinic
Space group	$P2_1$
a/(Å)	16.920(5)
b/(Å)	18.943(5)
c/(Å)	14.887(5)
α/(°)	90.000(5)
β/(°)	113.068(5)
γ/(°)	90.000(5)
Unit cell volume/(Å^3)	4390(2)
Z	2
T measurement/(K)	120
Density/(calculated)/(Mg m^{-3})	1.204
Absorption coefficient/(mm^{-1})	0.545
F (000)	1728
Crystal size/(mm^3)	0.5 x 0.1 x 0.5
Theta range for data collection/(°)	3.56 to 30.00
Index ranges	$-19 \leq h \leq 21, -23 \leq k \leq 23, -18 \leq l \leq 17$
Reflections collected	33046
Independent reflections	16223 [R(int) = 0.0403]
Completeness to theta = 30.00° (%)	97.0
Goodness-of-fit on F^2	1.004
Final R indices [$I > 2 \sigma(I)$]	R1 = 0.0905, wR2 = 0.2341
R indices (all data)	R1 = 0.1370, wR2 = 0.2644
Absolute structure parameter	0.50(3)
Largest diff. peak and hole	0.824 and -0.378 e.Å-3

Table 2. Selected bond lengths [Å] and angles [°] for [Cu₂(bopba)]

Cu(1)-O(19)	1.884(9)	Cu(20)-N(33)	1.892(7)
Cu(1)-N(07)	1.886(9)	Cu(20)-N(26)	1.925(10)
Cu(1)-N(14)	1.926(7)	Cu(20)-O(21)	1.932(6)
Cu(1)-O(02)	1.962(9)	Cu(20)-O(38)	1.982(7)
O(02)-C(03)	1.399(17)	O(21)-C(22)	1.272(14)
C(03)-O(04)	1.229(12)	C(22)-O(23)	1.274(14)
C(03)-C(05)	1.413(16)	C(22)-C(24)	1.641(15)
C(05)-O(06)	1.266(12)	C(24)-O(25)	1.253(14)
C(05)-N(07)	1.329(12)	C(24)-N(26)	1.310(16)
N(07)-C(08)	1.392(12)	N(26)-C(27)	1.429(12)
C(10)-C(29)	1.473(8)	C(32)-N(33)	1.423(12)
C(13)-N(14)	1.360(11)	N(33)-C(34)	1.250(13)
N(14)-C(15)	1.406(11)	C(34)-O(35)	1.255(13)
C(15)-O(16)	1.210(9)	C(34)-C(36)	1.595(14)
C(15)-C(17)	1.525(13)	C(36)-O(37)	1.263(10)
C(17)-O(18)	1.238(12)	C(36)-O(38)	1.305(11)
C(17)-O(19)	1.247(13)		
O(19)-Cu(1)-N(07)	169.5(3)	N(33)-Cu(20)-N(26)	83.0(4)
O(19)-Cu(1)-N(14)	86.1(3)	N(33)-Cu(20)-O(21)	168.0(3)
N(07)-Cu(1)-N(14)	83.6(4)	N(26)-Cu(20)-O(21)	85.1(4)
O(19)-Cu(1)-O(02)	104.9(3)	N(33)-Cu(20)-O(38)	84.3(3)
N(07)-Cu(1)-O(02)	85.5(4)	N(26)-Cu(20)-O(38)	167.3(3)
N(14)-Cu(1)-O(02)	169.0(4)	O(21)-Cu(20)-O(38)	107.5(3)
C(03)-O(02)-Cu(1)	105.4(7)	C(22)-O(21)-Cu(20)	115.9(7)
O(04)-C(03)-O(02)	110.7(12)	O(21)-C(22)-O(23)	132.4(11)
O(04)-C(03)-C(05)	126.6(14)	O(21)-C(22)-C(24)	112.1(10)
O(02)-C(03)-C(05)	120.1(9)	O(23)-C(22)-C(24)	112.5(11)
O(06)-C(05)-N(07)	126.4(10)	O(25)-C(24)-N(26)	130.1(11)
O(06)-C(05)-C(03)	121.8(9)	O(25)-C(24)-C(22)	117.1(11)
N(07)-C(05)-C(03)	111.0(10)	N(26)-C(24)-C(22)	111.8(11)
C(05)-N(07)-C(08)	130.6(9)	C(24)-N(26)-C(27)	128.7(10)
C(05)-N(07)-Cu(1)	116.0(7)	C(24)-N(26)-Cu(20)	114.8(8)
C(08)-N(07)-Cu(1)	113.4(6)	C(27)-N(26)-Cu(20)	116.5(6)
C(09)-C(08)-N(07)	125.5(9)	C(28)-C(27)-N(26)	126.7(8)
C(13)-C(08)-N(07)	115.7(8)	C(32)-C(27)-N(26)	109.4(9)
C(09)-C(10)-C(29)	125.9(7)	C(28)-C(29)-C(10)	120.0(7)
C(11)-C(10)-C(29)	120.1(7)	C(30)-C(29)-C(10)	120.8(7)
N(14)-C(13)-C(12)	130.9(8)	C(31)-C(32)-N(33)	126.0(9)
N(14)-C(13)-C(08)	111.8(7)	C(27)-C(32)-N(33)	117.6(8)
C(12)-C(13)-C(08)	117.3(8)	C(34)-N(33)-C(32)	127.9(8)
C(13)-N(14)-C(15)	132.1(7)	C(34)-N(33)-Cu(20)	118.4(7)
C(13)-N(14)-Cu(1)	115.5(6)	C(32)-N(33)-Cu(20)	113.4(6)
C(15)-N(14)-Cu(1)	112.3(6)	O(35)-C(34)-N(33)	132.7(10)
O(16)-C(15)-N(14)	127.4(9)	O(35)-C(34)-C(36)	116.3(8)
O(16)-C(15)-C(17)	124.6(9)	N(33)-C(34)-C(36)	110.5(10)
N(14)-C(15)-C(17)	108.0(8)	O(37)-C(36)-O(38)	121.8(10)
O(18)-C(17)-O(19)	125.4(9)	O(37)-C(36)-C(34)	122.4(9)
O(18)-C(17)-C(15)	114.4(10)	O(38)-C(36)-C(34)	115.5(8)
O(19)-C(17)-C(15)	119.9(10)	C(36)-O(38)-Cu(20)	110.5(6)
C(17)-O(19)-Cu(1)	113.1(7)		

have been omitted. The molecule consists of two [Cu(opba)]²⁻ monomers connected through a covalent bond between the C(10) and C(29) atoms from the phenyl moiety, leading to a copper dimer. This [Cu₂(bopba)]⁴⁻ dimer is almost flat with RMS deviation of fitted atoms positions from the best plane equal to 0.11 Å. The largest deviation is about –0.28 Å for O(16) and O(37) atoms. The copper atoms are in a square planar environment with average values of the Cu-N and Cu-O bond lengths equal to 1.91(2) Å and 1.94(3) Å respectively. The corresponding average bond angles for O-Cu-O and N-Cu-N are 106(2)° and 83.3(2)° respectively. The intramolecular Cu(01)-Cu(20) distance is equal to 11.796 Å and the inter-molecular Cu(1)-Cu(1)ⁱ distance (i = x, 1 - y, –0.5 + z) along the *c* axis is equal to 7.483 Å. Selected bond lengths and angles are listed in Table 2. The [Cu₂(bopba)]⁴⁻

structure and packing are sketched in Figure 3. The $Cu_2(bopba)$ packing along the *c* direction shows molecules rotated by about 100° in consecutive layers giving rise to a sort of zigzag arrangement represented in Figure 3b.
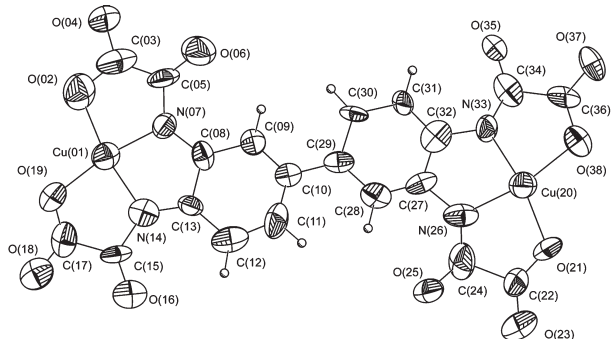

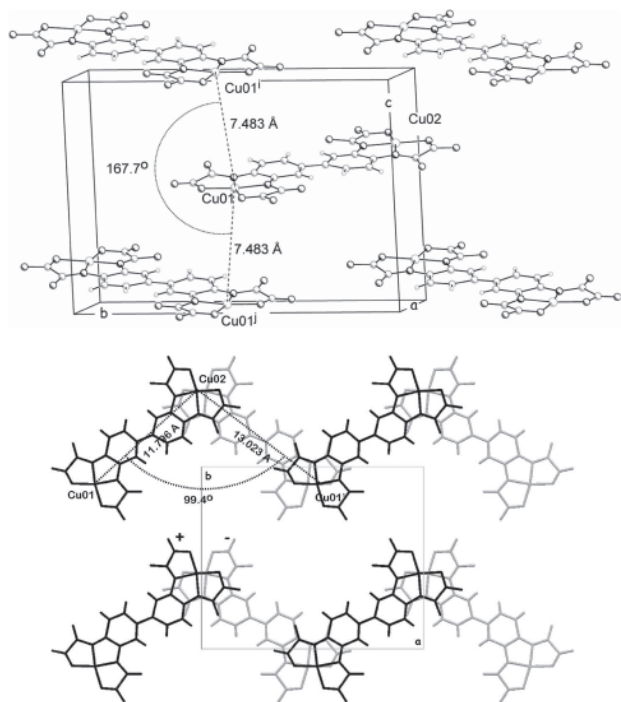**Figure 2.** $[Cu_2(bopba)]^{4-}$ dimer structure projection.

Figure 3. (a) $[Cu_2(bopba)]^{4-}$ dimer structure projection (i = x, 1 - y, –0.5 + z; j = x, 1 - y, 0.5 + z). (b) $[Cu_2(bopba)]^{4-}$ molecules stacked along the *c* direction. The + and - indicate molecules with different z axis quotes. For sake of simplicity the tetrabuthylammonium molecules were omitted.

Magnetic properties

The magnetic susceptibility data for compound **1** is presented in Figure 4 in the form of the $\chi_M T$ *versus* T plot, χ_M being the molar magnetic susceptibility and T the temperature. The $\chi_M T$ value at room temperature is close to 0.7 emu K mol^{-1}, near the expected value for a two independent ½ spin system, 0.75 emu K mol^{-1}. When T is lowered, $\chi_M T$ is almost flat with a small upward curvature reaching a maximum at 21 K with $\chi_M T$ = 0.71 emu K

mol^{-1} and then decreases abruptly below 4 K. This uncommon behavior, reproduced in three samples of different syntheses, may indicate the presence of competing short range ferromagnetic and antiferromagnetic interactions and a clear overall antiferromagnetic behavior setting in at low temperatures. The reciprocal susceptibility *versus* temperature, shown in the inset of the Figure 4, indicates the presence of average ferromagnetic interactions, with a positive Curie-Weiss temperature of about 0.5 K. The presence of ferromagnetic interactions was also observed in other copper(II) complexes,[20] with a similar positive value for the Curie-Weiss temperature.
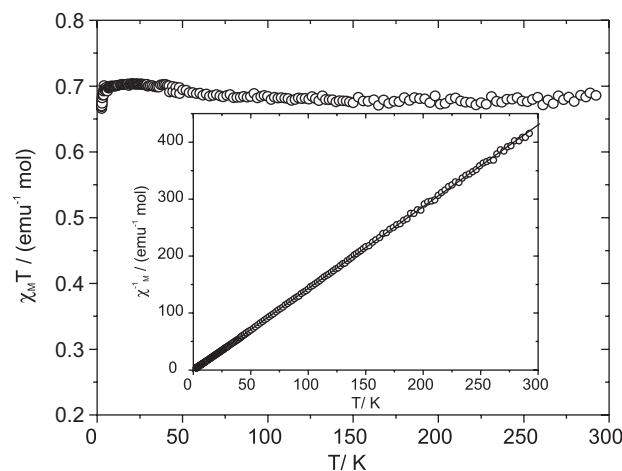

Figure 4. $\chi_M T$ *versus* T plot for (**1**). Inset shows $1/\chi_M$ *versus* T plot.

The magnetic susceptibility data for **2** is presented in Figure 5 in the form of $\chi_M T$ *versus* T. At room temperature the $\chi_M T$ value is equal to 1.93 emu K mol^{-1}, which is smaller than the expected value for six magnetically non-interacting S= ½ spins (two copper(II) ions and four nitroxide radicals), 2.25 emu K mol^{-1}. As the temperature is decreased, $\chi_M T$ increases to reach a maximum at 6 K with $\chi_M T$=2.21 emu K mol^{-1} and then decreases abruptly below 6 K.
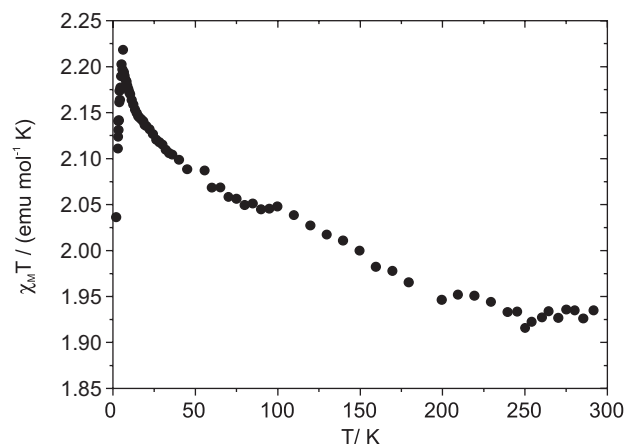

Figure 5. Temperature dependence of the $\chi_M T$ for $(pEtRad)_4[Cu_2(bopba)]$ (**2**).

The magnetization data obtained at 1.8 K are shown in Figure 6 in the form of M *versus* H, where M is the magnetization and H is the applied field. The magnetization reaches a maximum value of 5.6 μ_B at 60 kOe, which is close to the expected saturation value for six ½ spins. The inset of Figure 6 shows the measurement done at 1.8 K and at 4 K in the form of M *versus* H/T. The two curves do not superpose, which indicates the presence of antiferromagnetic interactions between the spin carriers at these temperatures.
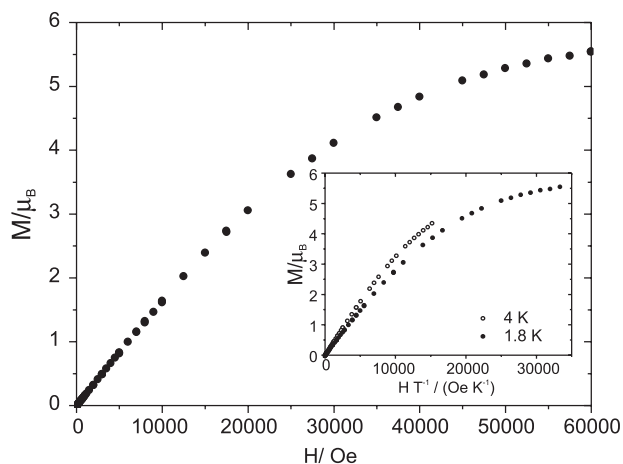

Figure 6. Field dependence of the magnetization for (pEtRad)$_4$[Cu$_2$(bopba)] (**2**).

Both the M *versus* H and χ_MT *versus* T measurements allow to speculate about the kind of magnetic interactions operative between the magnetic centers present in the (pEtRad)$_4$[Cu$_2$(bopba)] compound. The value of the χ_MT *versus* T at 300 K is slightly smaller than expected for six free spins. This behavior was also observed in other compounds with copper(II) and nitronyl nitroxide radicals,[14,21] and may be related to a smaller value of g or antiferromagnetic interactions.

On the other hand, the magnetic behavior between 300 K and 6 K observed in the χ_MT *versus* T plot (upward curvature in Figure 5) clearly shows the presence of ferromagnetic interactions. In order to understand this behavior, one has to recall on how metal transition ions generally interact with nitronyl nitroxide radicals. These are stable organic radicals that have an N-O group with an unpaired electron in a π^* orbital, equally shared by nitrogen and oxygen atoms.[22] When the nitronyl nitroxide binds through the oxygen atom, the four possible relative orientations of the magnetic orbitals are shown on Figure 7.

In the case a), if the M-O-N angle is equal to 180°, the two orbitals π^* and $d_{x^2-y^2}$ are orthogonal to each other and in this case the spins have to be parallel, leading to a ferromagnetic coupling. This is an uncommon situation that occurs in copper(II)-nitroxide complexes when the
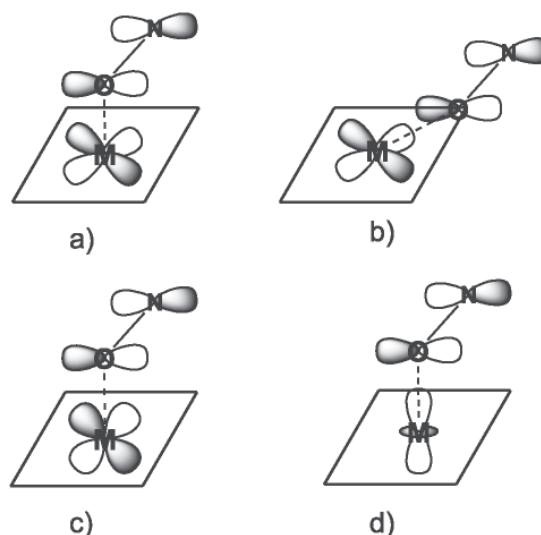

Figure 7. Schematic representation of the interactions between the magnetic orbitals of a metal ion and of a nitroxide radical.

radical is in an axial coordination site. In copper(II) complexes, when the Cu-O-N angle increases, the angle determined by the projection of the O-N bond on the XY plane with the X axis, as well as the dihedral angle between the Cu-O-N and the nitroxide plane, have an important influence on the exchange integral value, but not on its sign, which remains positive, leading to a ferromagnetic interaction.[23,7]

Case b) is expected in copper(II)-nitroxide complexes when the radical coordinates in an equatorial site. If the M-O-N angle is different from 180°, the coupling is antiferromagnetic.

Cases c) and d) are found in complexes of nickel(II), cobalt(II) and manganese(II), with the observed coupling being strongly antiferromagnetic.

The ferromagnetic coupling observed in the (pEtRad)$_4$[Cu$_2$(bopba)] compound may be explained by the coordination of each copper(II) ion with one nitronyl nitroxide radical as in case a) above. This was previously reported in a similar compound[14] where the magnetic data were fitted by considering a ferromagnetic interaction between the copper(II) ion and one NIT radical. The value reported for the coupling constant was J=31 cm^{-1}. We tried first to fit our data with this same model, *i.e.* one radical ferromagnetically coupled to each copper(II) and the others uncoupled. The next trial was to add an antiferromagnetic coupling between one uncoupled radical to the other free radical of the neighboring molecule. In both cases it was not possible to obtain a satisfactory fit, though we could estimate that the ferromagnetic coupling constant value is around 23 cm^{-1} in either case. Unfortunately the crystal structure could not be determined and other models of interacting spins would be too

speculative. Our results suggest that, in the $(pEtRad)_4[Cu_2(bopba)]$ compound, competing short range ferromagnetic and antiferromagnetic interactions are present with a slight predominance of ferromagnetic interaction at high temperatures. At low temperature other weak antiferromagnetic interactions, presumably of intermolecular origin, become important, leading to a decrease of $\chi_M T$ below 6 K. The abrupt character of this behavior suggests that a long range order may be established and a phase transition to a three-dimensional magnetic order may occur below this temperature.

Conclusions

We presented the crystallographic structure and the magnetic properties of a promising copper(II) building-block (compound **1**) that was already used to prepare a new molecular ferrimagnetic compound[12] by substitution of the tetrabuthylammonium cation with a manganese(II) ion. A new compound was synthesized and characterized by replacing the NBu_4^+ species by a cationic nitronyl nitroxide radical. The magnetic behavior of this compound indicated the presence of competing short range ferromagnetic and antiferromagnetic interactions. In order to explain fully the magnetic behavior of this compound, the knowledge of the crystalline structure is necessary and new efforts to obtain single crystals are in progress.

Acknowledgments

Supplementary Information

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 615466. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK ; fax: +44 1223 336033 ; or e-mail: deposit@ccdc.cam.ac.uk).

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