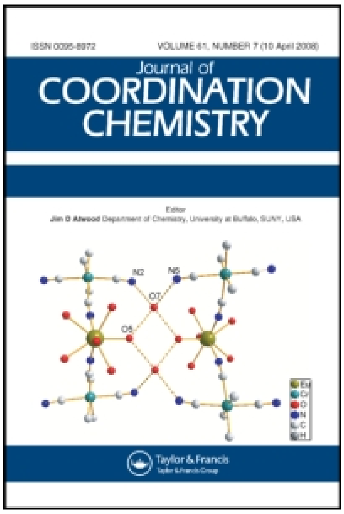

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Crystal Structure and Magnetic Properties of a Copper(II) Chloride Complex with Nitronyl Nitroxide

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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A COPPER(II) CHLORIDE COMPLEX WITH NITRONYL NITROXIDE

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A new compound [Cu(NITPhCH$_3$)$_2$Cl$_2$] (NITPhCH$_3$ 2-(4-methyl-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide) has been characterized spectroscopically. A crystal structure analysis has shown the copper ion to be planar, coordinated by two chlorine atoms and two oxygen (nitroxyl) atoms. Based on magnetic susceptibility measurements the compound was found to exhibit a moderately strong antiferromagnetic interaction ($J = -107.44\,\mathrm{cm}^{-1}$) between copper(II) and the radical.

Keywords: Nitronyl nitroxide; Copper(II) complex; Crystal structure; Magnetic interactions

INTRODUCTION

Transition metal ions and stable organic radicals, such as the nitroxides, can form clusters containing variable numbers of spins [1 – 8]. For instance, finite clusters containing from 2 to 12 spins have been reported, as well as infinite arrays. The simplest clusters comprise one metal ion directly bound to either one or two nitronyl nitroxides, and a study of their magnetic properties provided basic information on the nature of the exchange interaction between metal ions and radicals, basic for the design [9, 10] of one-dimensional ferrimagnets that order as three-dimensional ferromagnets

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below 10 K [11 – 13]. The main limitations found so far in the use of nitronyl nitroxides, in order to synthesize bulk ferro- or ferrimagnets, are related to their weak Lewis basicity and they require relatively strong Lewis acids to form stable complexes. This is usually accomplished by allowing nitroxides to react with metal hexafluoroacetylacetonates (hfac). However, the resulting metal-nitroxide units are well shielded from one another by the bulky CF_3 groups and consequently the magnetic ordering of materials including hfac co-ligands occurs at low temperatures. Although the use of smaller co-ligands may be an effective approach for increasing the transition temperature of materials including metal-nitroxide units, little work has yet been devoted to this type of approach.

With these considerations in mind, we obtained a compound of formula $[Cu(NITPhCH_3)_2Cl_2]$ ($NITPhCH_3$ = 2-(4-methyl-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), which contains three spins. We report here the crystal structure and magnetic properties of the compound.

EXPERIMENTAL

Syntheses of Complex

All reagents were of analytical grade and were used without further purification. The $NITPhCH_3$ radical was prepared according to the literature method [14].

Some 26.9 mg (0.1 mmol) of $CuCl_2$ was dissolved in absolute ethanol (10 cm^3), and 50.6 mg (0.2 mmol) of $NITPhCH_3$ was added. The solution was stirred for 10 mins and stored at $-4°C$. Well-shaped red crystals were obtained after 1 day. Yield: 53%. Calcd. For $C_{28}H_{38}O_4N_4Cl_2Cu$(%): C, 53.4; H, 6.1; N, 8.9 Found: C, 53.7; H, 6.3; N, 8.7.

Physical Measurements

Elemental analyses were carried out with a Perkin Elmer model 240 instrument. The electronic spectrum was measured with a Perkin Elmer Hitachi 240 spectrophotometer. The powder ESR spectrum was recorded on a JESFEIXG ESR spectrometer using X-band frequencies. IR spectra (KBr pellets) were measured with a Shimadzu IR-408 infrared spectrophotometer in the 4000 – 600 cm^{-1} region. Magnetic susceptibility measurements of a crystalline sample were carried out in the temperature range 2 – 300 K using a vibrating sample magnetometer (Maglab 2000). Experimental susceptibilities were corrected for diamagnetism of the constituent atoms.

Crystallographic Data Collection and Structure Determination

A red crystal of dimensions $0.30 \times 0.25 \times 0.20$ mm was mounted on a glass fibre in random orientation. Determination of the unit cell and data collection were performed on a computer-controlled Bruker SMART 1000 diffractometer. Some 3186 independent reflections in four octants $(h, -13-8; k, -14-15; l, -12-15)$ with $2.17 \leq \theta \leq 26.34^\circ$ were collected at

TABLE I Crystallographic data and data-collection parameters for the complex

Formula	$C_{28}H_{38}Cl_2CuN_4O_4$
Formula weight	629.06
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.957(1)
b/Å	12.565(1)
c/Å	12.070(1)
$\beta/^\circ$	109.90(2)
V/Å^3	1562.4(3)
Z	2
μ/mm^{-1}	0.908
R	0.041
R_w	0.110
Temperature of data collection/K	298(2)
Measured/independent reflections	7203/3186 [$R(int) = 0.033$]

TABLE II Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å$^2 \times 10^3$] for the complex

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	5000	10000	0	35(1)
Cl(1)	3037(1)	10538(1)	−1057(1)	55(1)
O(1)	4494(2)	10288(2)	1404(1)	45(1)
N(1)	5321(2)	10420(2)	2468(2)	39(1)
C(1)	5722(2)	9666(2)	3287(2)	38(1)
N(2)	6540(2)	10143(2)	4278(2)	47(1)
C(3)	5761(3)	11521(2)	2916(2)	44(1)
C(4)	5356(2)	8550(2)	3190(2)	40(1)
C(5)	4198(3)	8195(2)	2352(2)	50(1)
C(6)	3872(3)	7125(2)	2313(2)	56(1)
C(7)	4644(3)	6394(2)	3086(2)	57(1)
C(8)	5796(3)	6750(2)	3900(3)	53(1)
C(9)	6157(3)	7804(2)	3952(2)	44(1)
C(10)	4258(5)	5233(3)	3062(4)	93(1)
C(11)	7027(4)	11948(2)	5115(3)	59(1)
C(12)	8214(3)	11169(3)	3860(3)	62(1)
C(13)	6096(4)	12153(2)	1985(3)	57(1)
C(14)	4602(3)	12022(2)	3156(3)	61(1)
O(2)	7006(3)	9720(2)	5287(2)	77(1)
C(2)	6910(3)	11255(2)	4045(2)	46(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

293(2) K using MoKα radiation with a graphite monochromator ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares methods using the SHELX-97 package [15] of programs. The final R and R_w values were 0.041 and 0.110, respectively. Crystallographic data and refinement parameters are listed in Table I. Final atomic coordinates for non-hydrogen atoms are given in Table II and full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

Description of the Crystal Structure

The crystal structure of the complex consists of discrete four-coordinate monomers. The molecule is centrosymmetric, the copper atom being located at a centre of symmetry in the cell. A view of the molecule is shown in Figure 1. The copper ion is bound to two chlorine ions with a Cu—Cl distance of 2.2005(6) Å and two nitroxyl oxygen atoms with a Cu—O bond distance of 1.987(2) Å. These values are well within the ranges previously observed for chlorine-copper [16] and copper-nitroxyl [17, 18] bond lengths.

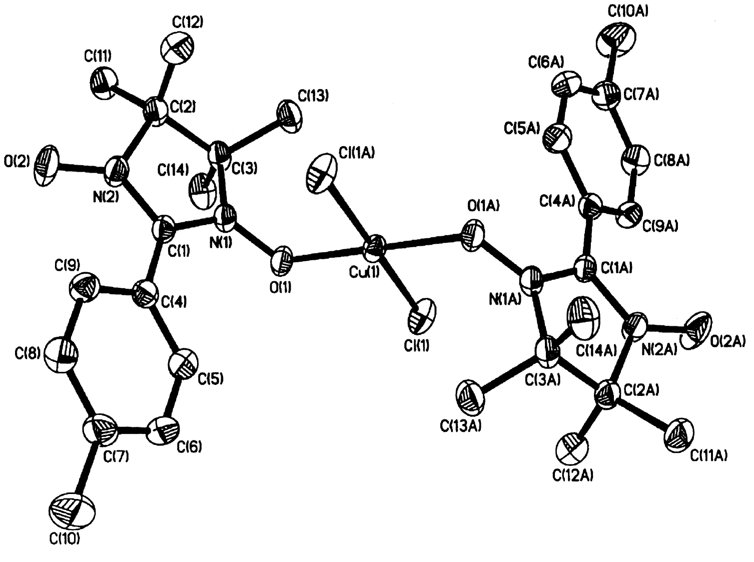

FIGURE 1 ORTEP drawing of the compound with the atom numbering scheme.

In the complex, the coordination plane is nearly perpendicular to the mean plane of the five-membered nitronyl nitroxide ring (84.3°). The Cu—O(1)—N(1) angles is 124.05(1)°, close to the value reported for some other metal-nitroxyl coordinated compounds [8, 17, 18]. The five-membered nitronyl ring is thus bent towards the chloride ion. The N(1)—O(1) bond length (1.305(2) Å) is longer than the N(2)—O(2) one (1.267(3) Å) in the complex. Taking into account that the two N—O bonds are equal in the free radical [19], this indicates a transfer of spin density from the *N*-oxyl-*N*-oxide system toward the copper ion. Selected bond distances and bond angles are given in Table III.

Spectroscopic and Magnetic Properties

Infrared spectra of the complex exhibits two characteristic strong bands. The N—O stretching vibrations observed at 1375 cm^{-1} for the free $\mathrm{NITPhCH_3}$ radical is shifted to lower frequencies (1355 cm^{-1}) in the complex as a result of coordination of the oxygen atom of the N—O group. Electronic spectra of the complex in ethanol are similar to that of a solution of the pure radical except for a slight shift (about 4 nm). The absorption can be attributed to the $\pi \rightarrow \pi^*$ transition of the benzene ring (290 nm) and to the $\pi \rightarrow \pi^*$ transition of the ONCNO of the radical at 362 nm. In the visible range, a very broad band centred around 580 nm can be attributed to d – d transitions of the Cu(II) ion. The powder X-band ESR spectrum at room temperature and 110 K are typical of square planar S = 1/2 spin system [20] with $g_{xx} = 2.01$, $g_{yy} = 2.05$, $g_{zz} = 2.10$. According to Kambe's approach [21], three individual spins ($S_1 = S_2 = S_3 = 1/2$) couple to yield the total spin states S = 1/2, 1/2 and 3/2.

Magnetic susceptibility data were collected on a crystalline sample in the temperature range 2 – 300 K. The variations of χ_M and μ_{eff} *vs.* T are represented in Figure 2. The effective magnetic moment per molecule of the complex decreases with temperature from 2.89 B.M. at 300 K to 1.98 B.M. at

TABLE III Selected bond distances (Å) and bond angles (°) for the complex

Cu(1)—O(1)	1.9873(16)	N(2)—C(2)	1.507(3)
Cu(1)—Cl(1)	2.2005(6)	N(1)—C(3)	1.505(3)
O(1)—N(1)	1.305(2)	C(1)—N(2)	1.365(3)
N(1)—C(1)	1.331(3)	N(2)—O(2)	1.267(3)
O(1)—Cu(1)—O(1)′	180.0	N(1)—O(1)—Cu(1)	124.05(14)
O(1)—Cu(1)—Cl(1)	86.41(5)	O(1)—N(1)—C(1)	125.7(2)
Cl(1)—Cu(1)—O(1)′	93.59(5)	O(1)—N(1)—C(3)	120.03(18)
O(1)—Cu(1)—Cl(1)′	180.0	C(1)—N(1)—C(3)	113.76(18)

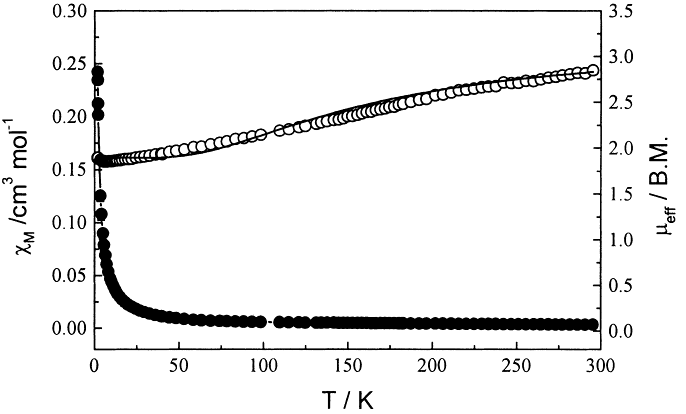

FIGURE 2 χ_M *versus* T and μ_{eff} *versus* T plots for the compound.

2 K, indicating the presence of moderately antiferromagnetic exchange interactions in this complex. The magnetic analysis was carried out with the susceptibility equation based on the Hamiltomian $\boldsymbol{H} = -2\mathrm{J}(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_2\boldsymbol{S}_3)$ for the three-spin system (R-Cu(II)-R, $S_R = S_{Cu} = 1/2$), where J is the exchange integral between Cu(II) and the radical.

$$\chi_M = \frac{Ng^2\beta^2}{4KT}\left[\frac{1+\exp(-2J/KT)+10\exp(J/KT)}{1+\exp(-2J/KT)+2\exp(J/KT)}\right] + N_\alpha$$

Least-squares fitting of the experimental data leads to $\mathrm{J} = -107.44\,\mathrm{cm}^{-1}$ and $g = 2.07$. The agreement factor as defined by $F = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \sum(\chi_M)_{obs}$ was 3.18×10^{-5}. This |J| value indicates the presence of a moderately strong intramolecular antiferromagnetic interaction in the complex.

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