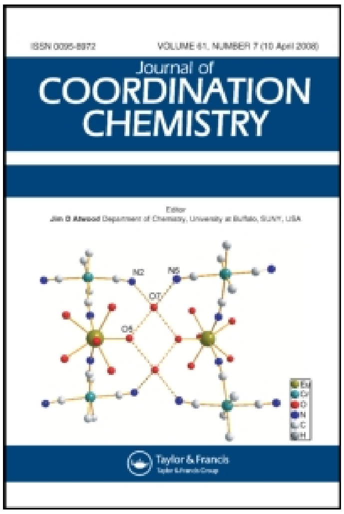

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Synthesis, crystal structure and magnetic properties of a new complex containing Cu(I) and radicals, $[Cu(imme2py)_2](ClO_4)$

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A new complex, $[Cu(imme2py)_2](ClO_4)$ (imme2py = 2-(2′-(6′-methylpyridyl))-4,4,5,5-tetramethyl-1H-imidazolyl-1-oxyl) has been synthesized and structurally characterized by X-ray diffraction methods. It crystallizes in the orthorhombic crystal system, space group $P_{2_12_12_1}$. The structure consists of $[Cu(imme2py)_2]^+$ cations and chloride anions. The coordination geometry about Cu(I) is tetrahedral with the four coordination sites being occupied by four nitrogen atoms. Magnetic measurements show intramolecular antiferromagnetic interactions between the imino nitroxides.

Keywords: Crystal structure; Imino nitroxide; Cu(I) complex; Magnetism

1. Introduction

There has been increasing interest in the study of molecular magnetic materials in recent years [1,2]. Pyridyl-substituted nitronyl nitroxide radicals have been employed as paramagnetic chelates in the design and synthesis of molecular magnetic materials [3,4]. The magnetic properties of complexes of nitronyl nitroxide radicals with paramagnetic metal ions have been studied [5–7]. Meanwhile, investigations of diamagnetic metal complexes with radicals have also attracted great attention due to antiferro- or ferro-magnetic interactions of radicals through the diamagnetic metal ions in the complexes [8–10].

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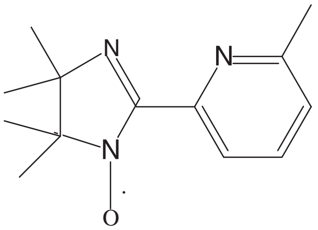

imme2py

In order to understand magnetic exchange interactions between the radicals through a diamagnetic metal ion, we have used a diamagnetic metal ion, Cu(I), as a linking agent between radicals to synthesize a complex imme2py–Cu–imme2py, (imme2py: 2-(2′-(6′-methylpyridyl))-4,4,5,5-tetramethyl-1H-imidazolyl-1-oxyl). We report here the synthesis, X-ray structure and magnetic properties of the title complex.

2. Experimental

2.1. *General*

All starting materials were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer instrument. The infrared spectrum was recorded on a Shimadzu IR spectrophotometer (model 408) in the 4000–600 cm^{-1} range, using KBr pellets. 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. *Synthesis of [Cu(imme2py)$_2$](ClO$_4$)*

2-(2′-(6′-Methylpyridyl))-4,4,5,5-tetramethyl-1H-imidazolyl-1-oxyl was prepared by a literature method [11,12]. The complex [Cu(imme2py)$_2$](ClO$_4$) was synthesized by the addition of imme2py (0.240 g, 1 mmol) and $Cu(ClO_4)_2$ (0.185 g, 0.5 mmol) to 40 cm^3 of ethanol solvent. The mixture was stirred for 1 h and then filtered; the clear filtrate was allowed to stand at room temperature for 7 d. Due to the ethanol solvent, the Cu(II) ion is reduced to Cu(I). Green crystals suitable for X-ray analysis were obtained (Anal. Found: C, 57.1; H, 4.2; N, 10.7. $C_{26}H_{36}N_6O_6ClCu$ calcd: C, 57.8; H, 4.8; N, 11.2%).

2.3. *X-Ray data collection and structure determination*

A green, single crystal of the complex having approximate dimensions $0.15 \times 0.10 \times 0.02$ mm, was mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the ω–ϕ scan technique in the range $1.73 \leq \theta \leq 25.04°$ with index ranges $-7 \leq h \leq 12$, $-18 \leq k \leq 18$, $-20 \leq l \leq 19$. A total of 12499 reflections were collected including 5347 independent ones ($R_{\mathrm{int}} = 0.3407$). A summary of the crystallographic data is given in table 1. The structure was solved by direct methods using

Table 1. Crystallographic data and refinement details for [Cu(imme2py)$_2$](ClO$_4$).

Empirical formula	$C_{26}H_{36}N_6O_6ClCu$
Formula weight	627.60
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	$a = 10.907$ (6) $b = 15.924$ (9) $c = 17.453$ (10)
Volume (Å^3), Z	3031 (3), 4
Calculated density (g cm^{-3})	1.375
Absorption coefficient (mm^{-1})	0.857
F(000)	1312
Crystal size (mm^3)	$0.15 \times 0.10 \times 0.02$
θ Range for data collection (°)	1.73–25.04
Limiting indices	$-7 \leq h \leq 12$, $-18 \leq k \leq 18$, $-20 \leq l \leq 19$
Reflections collected	12499
Independent reflection	5347 [R(int) = 0.3407]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5347/0/371
Goodness-of-fit on F^2	0.908
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0821$, $wR2 = 0.1673$
R indices (all data)	$R1 = 0.3284$, $wR2 = 0.2452$
Extinction coefficient	0.0148 (14)
Largest diff. peak and hole (e Å^{-3})	0.579 and −0.451

the SHELXS-97 program [13]. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. Full-matrix least-squares refinement on F^2 gave final agreement factors $R_1 = 0.0821$, $wR_2 = 0.1673$ $(I > 2\sigma(I))$; $R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|, wR_2 = (\sum w|F_0|^2 - |F_c|^2)^2/\sum(w|F_0|^2)^2, w = 1/[\sigma^2(F_0^2) + (0.0700P)^2 + 0.0000P]$ where $P = (F_0^2 + 2F_c^2)/3$. Positional parameters and selected bond distances and angles are given in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Crystal structure of [Cu(imme2py)$_2$](ClO$_4$)*

An ORTEP drawing of the [Cu(imme2py)$_2$]$^+$ ion is shown in figure 1. The Cu(I) ion is four-coordinate in a tetrahedral CuN$_4$ environment. The four coordination sites of the Cu(I) ion are occupied by four nitrogen atoms from two imme2py ligands. The Cu–N(imino nitroxide) bond lengths are 1.947(12) and 1.961(12) Å and are shorter than the Cu–N(pyridine) bond lengths (2.015(14) and 2.055(13) Å). The dihedral angle between the pyridyl ring and the ON–C–NO group is 8.3°. The dihedral angle between the two radical planes coordinated to the Cu(I) ion (Cu–N1–C3–N3–O1 and Cu–N5–C16–N6–O2) is 87.9°.

3.2. *Magnetic properties of [Cu(imme2py)$_2$](ClO$_4$)*

The magnetic susceptibilities, χ_M, of the title complex were measured in the range 5−300 K at 10000 G. Plots of μ_{eff} and χ_M *versus* T are shown in figure 2. The μ_{eff}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Cu(imme2py)$_2$](ClO$_4$).

Atom	*x*	*y*	*z*	*U*(eq)
Cu(1)	2440(2)	9527(1)	1519(1)	59(1)
N(1)	3609(11)	8763(10)	2013(7)	57(4)
N(2)	2250(14)	8505(8)	809(7)	55(4)
N(3)	4450(15)	7519(12)	2065(8)	68(5)
N(4)	2908(13)	10531(9)	879(8)	60(4)
N(5)	1101(11)	10263(10)	1824(7)	54(4)
N(6)	244(18)	11496(12)	1726(10)	94(6)
Cl(1)	2926(5)	4371(4)	240(4)	90(2)
O(1)	4750(11)	6782(9)	1894(7)	72(4)
O(2)	4(13)	12286(11)	1520(11)	118(6)
O(3)	2720(30)	5076(15)	−264(17)	264(14)
O(4)	2160(20)	3917(13)	−129(18)	250(15)
O(5)	2310(30)	4003(19)	923(15)	117(11)
O(6)	4117(12)	4026(8)	121(11)	135(7)
C(1)	4487(16)	8804(13)	2658(10)	68(6)
C(2)	5002(19)	7976(12)	2746(12)	73(6)
C(3)	3604(18)	7976(13)	1709(11)	61(6)
C(4)	2881(16)	7817(11)	1025(9)	49(5)
C(5)	2896(14)	7058(10)	653(9)	51(5)
C(6)	2140(20)	6980(17)	−3(13)	111(8)
C(7)	1550(20)	7660(15)	−215(13)	97(8)
C(8)	1532(18)	8361(13)	171(12)	79(7)
C(9)	851(17)	9132(10)	−96(10)	87(7)
C(10)	4630(30)	7468(14)	3486(13)	189(16)
C(11)	6370(20)	7863(14)	2653(16)	167(13)
C(12)	5380(30)	9512(14)	2452(15)	162(13)
C(13)	3730(20)	9155(17)	3362(11)	176(14)
C(14)	40(20)	10225(15)	2363(15)	93(7)
C(15)	−400(20)	11172(16)	2423(12)	93(7)
C(16)	1147(17)	10985(12)	1474(12)	61(5)
C(17)	2001(16)	11165(12)	873(10)	50(5)
C(18)	2148(18)	11889(13)	461(12)	79(7)
C(19)	3110(20)	11955(13)	−45(12)	91(8)
C(20)	3991(17)	11335(13)	−145(11)	74(6)
C(21)	3793(16)	10629(11)	331(11)	59(5)
C(22)	4621(19)	9864(13)	268(10)	106(8)
C(23)	150(30)	11600(20)	3091(13)	191(16)
C(24)	−1743(17)	11330(14)	2336(12)	120(9)
C(25)	−860(20)	9660(14)	1914(15)	138(10)
C(26)	350(20)	9802(15)	3077(12)	120(9)

Table 3. Selected bond lengths (Å) and angles (°) for [Cu(imme2py)$_2$](ClO$_4$).

Cu(1)–N(5)	1.947(12)	N(3)–O(1)	1.254(16)
Cu(1)–N(1)	1.961(12)	N(3)–C(3)	1.33(2)
Cu(1)–N(4)	2.015(14)	N(5)–C(16)	1.302(19)
Cu(1)–N(2)	2.055(13)	N(6)–O(2)	1.334(18)
N(1)–C(3)	1.360(19)	N(6)–C(16)	1.35(2)
N(5)–Cu(1)–N(1)	137.8(6)	O(1)–N(3)–C(3)	125.6(17)
N(5)–Cu(1)–N(4)	82.2(6)	O(1)–N(3)–C(2)	122.1(16)
N(1)–Cu(1)–N(4)	124.8(6)	C(21)–N(4)–Cu(1)	131.1(14)
N(5)–Cu(1)–N(2)	124.5(6)	C(17)–N(4)–Cu(1)	113.2(12)
N(1)–Cu(1)–N(2)	80.8(6)	C(16)–N(5)–Cu(1)	112.0(12)
N(4)–Cu(1)–N(2)	108.6(5)	C(14)–N(5)–Cu(1)	136.8(14)
C(3)–N(1)–Cu(1)	113.4(13)	O(2)–N(6)–C(16)	128.5(19)
C(1)–N(1)–Cu(1)	136.7(14)	O(2)–N(6)–C(15)	117.0(19)
C(4)–N(2)–Cu(1)	115.0(12)	C(8)–N(2)–Cu(1)	132.5(13)

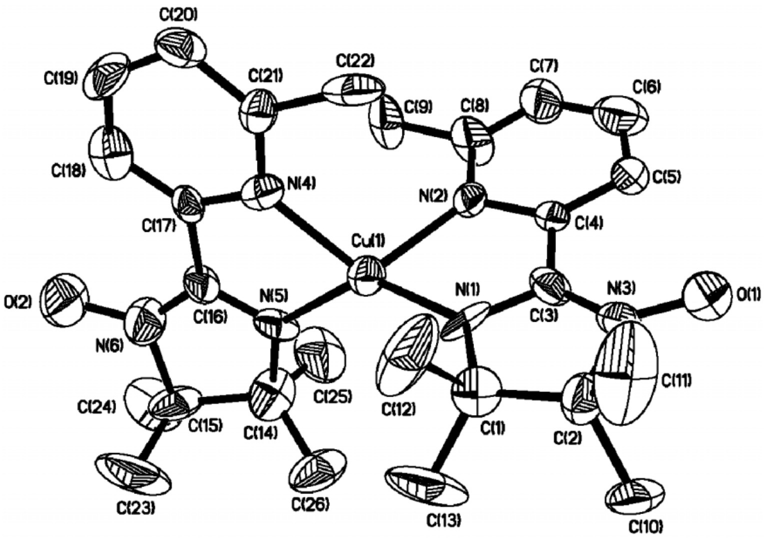

Figure 1. ORTEP drawing of the $[Cu(imme2py)_2]^+$ ion.

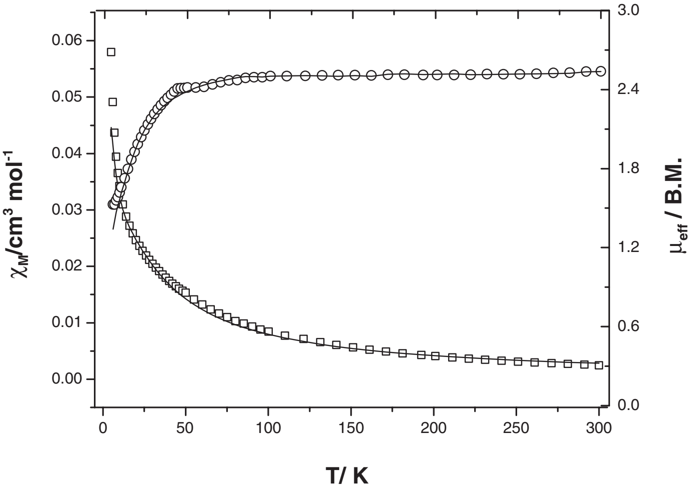

Figure 2. Temperature dependence of the molar magnetic susceptibility χ_M (□) and μ_{eff} (○) for $[Cu(imme2py)_2](ClO_4)$.

value at room temperature is $2.54\,\mu_B$, which is higher than the spin-only value expected for two $S = 1/2$ uncoupled spin systems ($2.45\,\mu_B$). When the systems are cooled from 300 to approximately 50 K, μ_{eff} value decreases slowly, and below approximately 50 K, μ_{eff} decreases rapidly reaching a value of $1.53\,\mu_B$ and implying the existence of weak antiferromagnetic spin exchange interactions between the imino nitroxides.

For the imme2py–Cu(I)–imme2py complex, two paramagnetic centers are linked by a diamagnetic metal ion; analysis of the magnetic properties was performed using the Bleany–Bowers (dimer) model [14]. Magnetic data were fitted to the theoretical expression for the magnetic susceptibility described by the Heisenberg Hamiltonian $\hat{H} = -2J\,\hat{S}_1 \cdot \hat{S}_2$, where J is the interaction parameter between two paramagnetic centers, as follows.

$$\chi_{\mathrm{M}} = \frac{2Ng^2\beta^2}{KT}[3 + \exp(-2J/KT)]^{-1}$$

The best-fit parameters were $J = -14.7\,\mathrm{cm}^{-1}$, $g = 1.99$ with $R = 4.20 \times 10^{-3}$, where R is defined as $R = \sum[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{calc}}]^2 / \sum(\chi_{\mathrm{M}})^2_{\mathrm{obs}}$.

The results indicate that the diamagnetic metal ion provides an orbital pathway for interradical exchange. Because the dihedral angle between the two radical planes deviates from 90°, the two radical magnetic orbitals are not strictly orthogonal. The weak antiferromagnetic spin exchange interactions between the imino nitroxides are mediated by the Cu(I) ion.

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Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 249377. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (Fax:+44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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