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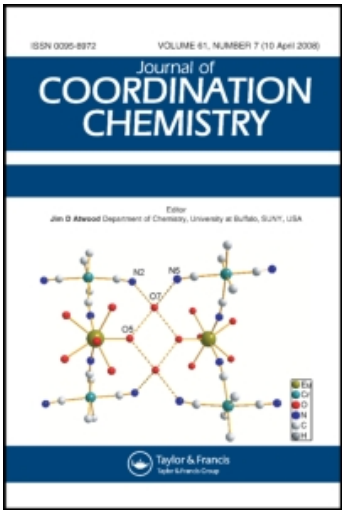

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A novel one-dimensional copper(II) imino nitroxide polymer

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A novel one-dimensional copper(II) imino nitroxide polymer

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A copper(II) complex $[Cu(im2\text{-}py)(4,4'\text{-}bipy)(NO_3)](NO_3)\cdot 1.5H_2O$ (im2-py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl; 4,4′-bipy = 4,4′-bipyridyl) has been synthesized by reaction of $Cu(NO_3)\cdot 3H_2O$ with im2py and 4,4-bipyridyl in methanol solution. Its crystal structure has been determined by X-ray diffraction. The structure shows that each copper ion is coordinated by a bidentate imino nitroxide radical, two 4,4′-bipyridyl ligands and a nitrate group to form a distorted square pyramidal environment. The crystal structure consists of chains of copper ions linked by 4,4′-bipyridyl.

Keywords: Imino nitroxide; Copper(II); Crystal structure

1. Introduction

The design and synthesis of one-dimensional magnetic chain complexes is an active area of magnetic materials research [1]. Nitroxide radicals, including nitronyl and imino nitroxides, are heavily-studied paramagnetic ligands due to their exceptional stability and versatility in terms of coordination properties [2, 3]. The use of bridging ligands in combination with the metal ions and nitroxide radicals has attracted much interest. For example, N_3^-, SCN^-, $N(CN)_2^-$ and terephthalato dianions have been used in the design of one-dimensional (1D) or multidimensional magnetic materials [4–9]. It is known that 4,4′-bipyridyl is a good bridging ligand and it has been extensively used in the synthesis of framework structures [10, 11] and many different structural motifs (ladder, zig-zag, diamond, railroad, brick wall, hexagonal grid, square grid) can be generated with this ligand [12–17]. Here the use of 4,4′-bipyridyl

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Table 1. Crystallographic data and data-collection parameters for the complex.

Formula	$C_{22}H_{27}CuN_7O_{8.50}$
Formula weight	589.05
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.645(4)
b (Å)	13.683(4)
c (Å)	17.964(5)
β (°)	90.649(6)
V (Å^3)	3353.7(16)
Z	8
μ (mm^{-1})	1.339
$F(000)$	2440
Reflections collected/unique	13131/725 [$R_{int} = 0.1367$]
R	0.0718
Rw	0.1416

and the radical 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (im2-py) to synthesize $[Cu(im2\text{-}py)(4,4'\text{-}bipy)(NO_3)]NO_3 \cdot 1.5H_2O$, a 1D chain complex is reported.

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2. Experimental

All reagents were of analytical grade and used without further purification. The ligand (im2-py) was prepared according to the reported method [18].

2.1. *[Cu(im2-py)(4,4′-bipy)(NO$_3$)]NO$_3$·1.5H$_2$O (1)*

To an aqueous solution (5 cm^3) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.2416 g, 1 mmol) was added dropwise a methanolic solution (5 cm^3) of im2-py (0.2182 g, 1 mmol) with continuous stirring for 30 min. 4,4′-Bipyridyl (0.1922 g, 1 mmol) in methanol (5 cm^3) was then added dropwise. The mixture was filtered after 2 h at room temperature, and then the filtrate placed in a desiccator with diethylether. Red-brown crystals were deposited with time.

2.2. *Crystallography*

A crystal ($0.40 \times 0.20 \times 0.20$ mm^3) was selected and mounted on a glass fibre. Diffraction data were collected on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). A total of 13131 including 5725 independent reflections ($R_{int} = 0.1367$) was collected in the $2.71 < \theta < 25.03°$ range at room temperature. The structure was solved by direct methods using the SHELXS97 program [19]. A full-matrix least-squares refinement on F^2 was carried out using SHELXL97 [20] and the goodness-of-fit on F^2 was 0.995. Final agreement factors are $R_1 = 0.0781$ and $wR_2 = 0.1416$ ($I > 2\sigma(I)$). Maximum and minimum peaks in the final difference Fourier synthesis were 0.597 and -0.675 e Å^{-3}, respectively. Crystallographic data and refinement parameters are listed in table 1. Final atomic coordinates for non-hydrogen atoms are given in table 2. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data

Table 2. 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)	2938(1)	1201(1)	3463(1)	48(1)
O(1)	6443(4)	1835(4)	4330(4)	99(2)
N(1)	3908(4)	173(4)	3779(3)	40(2)
N(2)	4069(4)	2076(4)	3715(3)	38(1)
N(3)	5624(4)	2153(5)	4080(4)	62(2)
N(4)	1874(4)	224(4)	3167(4)	46(2)
N(5)	1984(4)	2234(4)	3132(4)	49(2)
N(11)	1928(7)	1159(7)	5258(4)	79(2)
O(11)	2523(4)	1199(5)	4772(4)	93(2)
O(12)	2080(7)	700(7)	5829(6)	179(4)
O(13)	1117(6)	1483(7)	5224(4)	141(3)

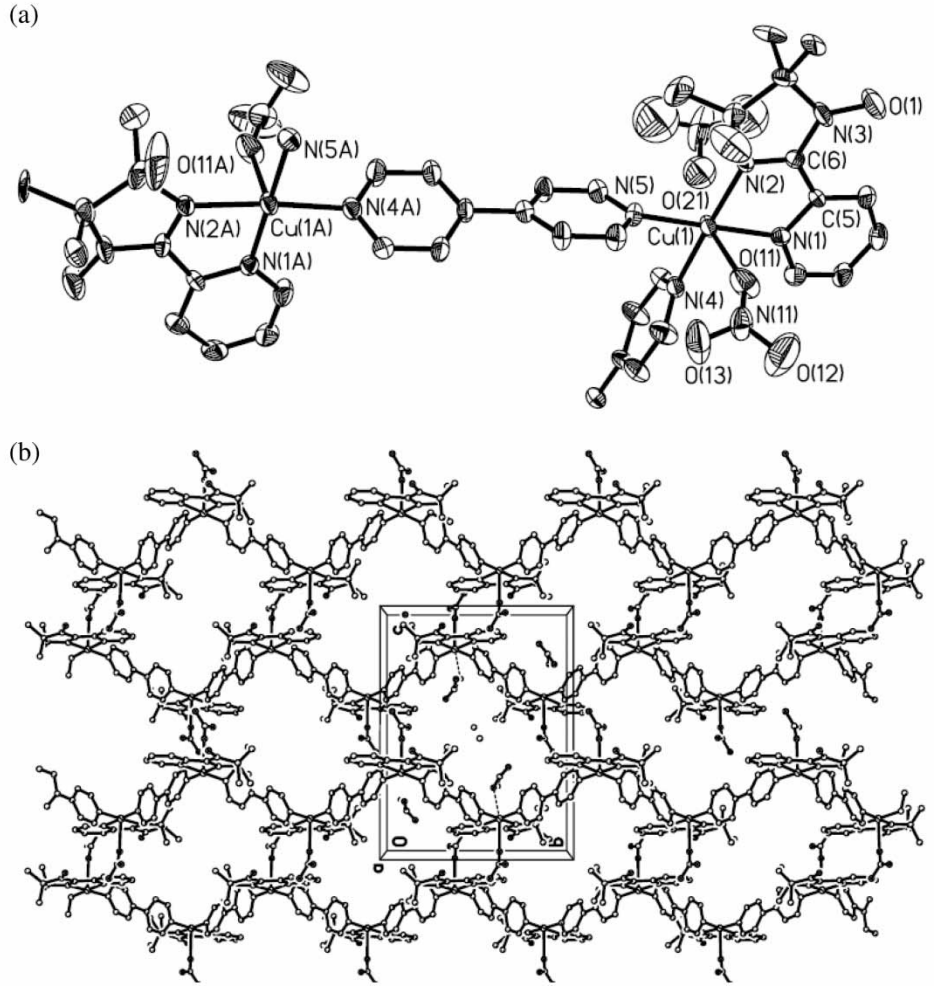

Figure 1. (a) An ORTEP view of the coordination geometry around Cu(II); (b) a perspective view of the infinite one-dimensional chains in the lattice.

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Table 3. Selected bond lengths (Å) and angles (°) for the complex.

Cu(1)–N(2)	2.001(5)
Cu(1)–N(5)	2.006(6)
Cu(1)–N(1)	2.009(5)
Cu(1)–N(4)	2.040(6)
Cu(1)–O(11)	2.425(7)
O(1)–N(3)	1.276(7)
N(11)–O(13)	1.194(8)
N(11)–O(11)	1.200(8)
N(11)–O(12)	1.219(9)
Cu(1)–O(21)	2.529(5)
N(2)–Cu(1)–N(5)	98.2(2)
N(2)–Cu(1)–N(1)	81.5(2)
N(5)–Cu(1)–N(1)	179.1(3)
N(2)–Cu(1)–N(4)	174.9(2)
N(5)–Cu(1)–N(4)	85.8(2)
N(1)–Cu(1)–N(4)	94.5(2)
N(2)–Cu(1)–O(11)	88.2(2)
N(5)–Cu(1)–O(11)	97.4(3)
N(1)–Cu(1)–O(11)	83.4(2)
N(4)–Cu(1)–O(11)	94.5(3)

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Centre (CCDC) as supplementary publication CCDC 267316. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

3. Results and discussion

An ORTEP plot of the molecular structure of [Cu(im2-py)(4,4′-bipy)(NO_3)](NO_3)·1.5H_2O is shown in figure 1. Selected bond distances and angles are given in table 3. Each Cu(II) ion is located in a distorted square pyramidal environment. The basal plane is occupied by two nitrogen atoms from im2-py [Cu(1)–N(1), Cu(1)–N(2); 2.009(5), 2.001(5) Å, respectively] and two bipyridyl nitrogen atoms [Cu(1)–N(4), Cu(1)–N(5); 2.040(6), 2.006(6) Å, respectively]. The apical position is occupied by an oxygen atom of a nitrate group [Cu(1)–O(11); 2.425(7) Å]. The copper center also is weakly coordinated by the free nitrate anion. Equatorial bond angles about Cu lie in the range 81.5–94.5° and Cu is displaced by 0.0341 Å towards the apical donor from the basal coordination plane. In the imino nitroxide radical, structural features are similar to those found in other copper(II)-imino nitroxide analogs [21]. The N1–C5–C6–N2–Cu group and the imino nitroxyl ring are all almost coplanar with a pyridyl ring, with dihedral angles of 2.8 and 2.5°, respectively. Each 4,4′-bipyridyl ligand is coordinated to two metal atoms, resulting in a one-dimensional chain which displays a zig-zag structure (figure 1). Among the chains, there are sited crystal water molecules.

Full crystallographic data are available from the authors upon request.

Acknowledgements

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