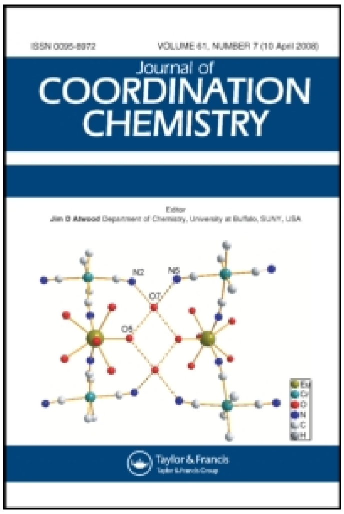

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Magnetic interactions in a new heterospin complex involving nitroxide radical and oxamido-bridged copper(II)

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A new binuclear copper(II) complex $[Cu_2(oxpn)(IM2py)_2](ClO_4)_2$, containing four spin carriers with pyridyl-substituted nitroxide radicals has been synthesized and characterized structurally and magnetically (oxpn = *N*,*N′*-*bis*(3-aminopropyl)oxamido, IM2py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl). The structure of the complex consists of centrosymmetric *trans* oxamido-bridged copper(II) binuclear units and nitroxide radicals. The coordination geometry around each copper atom is distorted square pyramidal and the apical position is occupied by a nitrogen atom of the imidazoline ring of a radical ligand. Magnetic analysis indicates that the complex exhibits strong antiferromagnetic coupling between copper(II) ions through the oxamido bridge and a ferromagnetic interaction between copper(II) ions and radical ligands. The magnetic behaviour is discussed with reference to the crystal structure.

Keywords: Copper; Oxamido-bridge; Nitroxide radical; Magnetic properties; Crystal structure

1. Introduction

Heterospin systems consisting of organic free radicals and paramagnetic metal ions constitute some of the most promising compounds useful for high Curie-temperature molecular-based magnets [1, 2]. Polynuclear complexes are of considerable interest for designing new magnetic materials and for investigating structure. One of the best strategies to design and synthesize polynuclear species is the 'complex as ligand' approach, *i.e.*, the use of mononuclear complexes that contain potential donor groups for another metal ion. A good example of 'complex ligands' is represented by mononuclear Cu(II) complexes of *N*,*N′*-*bis*(coordinating group)-substituted oxamides [3] such as [Cu(oxpn)] (scheme 1; oxpn = *N*,*N′*-*bis*(3-aminopropyl)oxamido). One of the most outstanding characters of these ligands is the easy transformation of *cis*-*trans* conformations upon coordination to metal ions (scheme 2), which makes it practical

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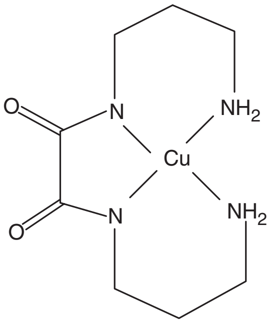
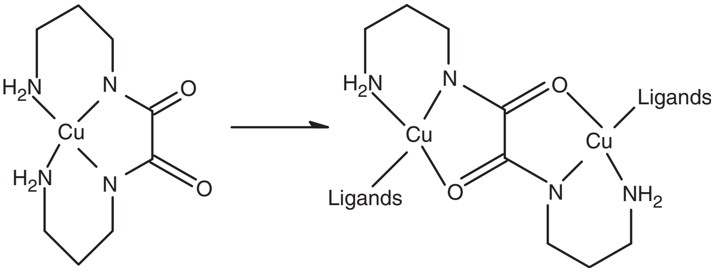


Scheme 1. The structure of [Cu(oxpn)].



Scheme 2. The transformation of cis-trans conformation.

to design tunable molecular materials with extended structures and desired properties [4, 5].

Oxamido-bridged bimetallic complexes and radical-metal complexes are two active research fields with respect to new molecular magnetic materials, so it would be interesting to obtain oxamido-bridged bimetallic complexes with stable pyridyl-substituted nitroxide radicals as terminal ligands. This combined synthetic approach should result in novel heterospin materials. Along this line, we have synthesized a new heterospin complex, $[Cu_2(oxpn)(IM2py)_2](ClO_4)_2$ (IM2py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl), which is a bimetallic oxamido-bridged complex involving pyridyl-substituted nitroxide radical ligands. Its structure and magnetic properties are reported below.

2. Experimental

2.1. *Physical measurements*

Elemental analyses (C, H, N) were carried out using a Perkin Elmer 240 system. IR spectra (KBr pellets) were recorded on a Bruker TENSOR 27/408 spectrophotometer in the range 4000–400 cm^{-1}. Magnetic susceptibility measurements of crystalline samples were carried out in the temperature range 2–300 K, using a Quantum

Design MPMS XL-7 magnetometer at a field strength of 2000G. Molar susceptibilities were corrected for the sample holder and diamagnetic contributions of all constituent atoms using Pascal's constants.

2.2. *Materials and synthesis*

All starting materials were of analytical grade and used as purchased without further purification. The mononuclear precursor Cu(oxpn) was synthesized according to a reported procedure [6].

The pyridyl-substituted radical IM2py was prepared according to a literature method [7].

To a green aqueous methanol solution (20 cm^3; 1 : 1 ratio) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol) and Cu(oxpn) (2 mmol) was added 4 mmol of IM2py dissolved in 10 cm^3 of methanol. The mixture was stirred for 2 h at room temperature and then filtered. The filtrate was kept at room temperature for a couple of days to give well-formed dark green crystals of the complex $[Cu_2(oxpn)(IM2py)_2](ClO_4)_2$. Anal. Calcd for $C_{16}H_{24}ClCuN_5O_6$ (%): C, 39.92; H, 5.02; N, 14.55. Found: C, 39.97; H, 5.10; N, 14.62.

2.3. *X-ray crystallography*

A single crystal of the complex was mounted on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the φ–ω scan mode. Unit cell parameters were determined fitting to data from $1.78 < \theta < 25.02°$. Details of data collection, crystallographic data and structure refinement parameters are summarized in table 1. The structure was solved using direct methods with SHELXS-97 [8], and refined with full-matrix least-squares techniques based on F^2 using SHELXL-97 [9]. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. All non-hydrogen atoms were refined anisotropically. Reliability factors are defined as $R_1 = \Sigma(|F_o| - |F_o|)/\Sigma|F_o|$ and the function minimized was $wR_2 = (\Sigma(|F_o|^2 - |F_o|^2)^2/\Sigma w|F_o|^2)^{1/2}$, with unit weights. Selected bond distances and angles are listed in table 2. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in table 3.

3. Results and discussion

3.1. *Description of the structure*

The complex $[Cu_2(oxpn)(IM2py)_2](ClO_4)_2$ consists of a binuclear centrosymmetric cation, $[Cu_2(oxpn)(IM2py)_2]^{2+}$, and two perchlorate anions. An ORTEP drawing of the cation is shown in figure 1. Two nitrogen atoms of pyridine rings and of the imidazoline ring, respectively, are coordinated to the *trans*-oxamido-bridged copper(II) unit, yielding a species with four spin carriers. Each copper(II) centre adopts a distorted

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{16}H_{24}ClCuN_5O_6$
Formula weight	481.39
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions (Å, °)	
a	15.699(4)
b	8.440(2)
c	15.859(4)
β	92.832(4)
Volume (Å^3)	2098.7(9)
Z, Calculated density (Mg m^{-3})	4, 1.524
Absorption coefficient (mm^{-1})	1.210
$F(000)$	996
Crystal size (mm^3)	$0.32 \times 0.21 \times 0.16$
θ range for data collection (°)	1.78–25.02
Limiting indices	$-12 \leq h \leq 18$, $-10 \leq k \leq 9$, $-18 \leq l \leq 18$
Reflections collected/unique	10886/3699 [$R(\text{int}) = 0.0272$]
Completeness to $\theta = 25.02$ (%)	100.0
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.329
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3699/204/339
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0411$, $wR_2 = 0.1042$
R indices (all data)	$R_1 = 0.0604$, $wR_2 = 0.1162$
Largest diff. peak and hole (e A^{-3})	0.466 and −0.329

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Cu(1)–N(3)	1.951(3)	N(5)–C(8)	1.351(5)
Cu(1)–O(2)	1.981(3)	C(1)–C(2)	1.516(7)
Cu(1)–N(4)	1.987(3)	C(1)–C(3)	1.527(8)
Cu(1)–N(5)	2.042(3)	C(1)–C(4)	1.558(6)
Cu(1)–N(2)	2.282(3)	N(3)–Cu(1)–O(2)	84.20(11)
O(1)–N(1)	1.264(4)	N(3)–Cu(1)–N(4)	94(2913)
O(2)–C(13)	1.278(4)	O(2)–Cu(1)–N(4)	16331(14)
N(1)–C(7)	1.382(5)	N(3)–Cu(1)–N(5)	171.94(12)
N(1)–C(1)	1.491(6)	O(2)–Cu(1)–N(5)	88.18(11)
N(2)–C(7)	1.282(4)	N(4)–Cu(1)–N(5)	92.25(12)
N(2)–C(4)	1.495(5)	N(3)–Cu(1)–N(2)	106.57(13)
N(3)–C(13)	1.289(5)	N(4)–Cu(1)–N(2)	98.50(13)
N(3)–C(14)	1.472(5)	N(5)–Cu(1)–N(2)	77.03(12)
N(4)–C(16)	1.473(5)	O(1)–N(1)–C(7)	126.6(4)
N(5)–C(9)	1.325(5)	O(1)–N(1)–C(1)	123.4(4)

Symmetry transformation used to generate equivalent atoms, #1: $-x+2$, $-y$, $-z+2$.

square pyramidal CuN_4O geometry. The basal plane comprises the carbonyl O(2), the amide N(4) and the amine N(3) (nitrogen atoms of the oxamide ligand), and N(5) of a pyridine ring. The nitrogen atom N(2) of the imidazoline radical ligand occupies the axial site. Cu(1)–N(2) is 2.282(3) Å, which is longer than that of the equatorial Cu(1)–N bond. The mean plane of the imidazoline ring makes a dihedral angle of 76.4° with the basal plane around Cu(1) and Cu(1A). The imidazoline ring of the nitroxide radical

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å} \times 10^3$) for the non-hydrogen atoms. U(eq.) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U (eq.)
Cu(1)	10608(1)	504(1)	8521(1)	47(1)
O(1)	8168(3)	1312(5)	6173(2)	107(1)
O(2)	10202(2)	974(3)	10972(1)	53(1)
N(1)	8615(3)	1906(4)	6778(2)	67(1)
N(2)	9630(2)	2062(4)	7802(2)	47(1)
N(3)	10739(2)	1368(4)	9661(2)	49(1)
N(4)	11662(2)	1516(4)	8133(2)	57(1)
N(5)	10404(2)	−677(4)	7405(2)	46(1)
C(1)	8453(3)	3504(5)	7138(3)	72(1)
C(2)	8770(5)	4671(7)	6498(4)	114(2)
C(3)	7499(4)	3695(8)	7253(5)	115(2)
C(4)	9029(3)	3389(5)	7965(3)	57(1)
C(5)	8557(4)	2899(7)	8747(3)	85(2)
C(6)	9541(4)	4883(6)	8159(4)	83(2)
C(7)	9351(2)	1275(5)	7154(2)	48(1)
C(8)	9785(3)	−138(5)	6856(2)	48(1)
C(9)	10849(3)	−1933(5)	7187(3)	61(1)
C(10)	10721(3)	−2683(6)	6418(3)	74(1)
C(11)	10096(4)	−2128(6)	5867(3)	77(1)
C(12)	9616(3)	−856(6)	6081(3)	65(1)
C(13)	10265(2)	671(4)	10188(2)	45(1)
C(14)	11268(3)	2718(5)	9954(2)	63(1)
C(15)	12072(3)	2876(6)	9467(3)	70(1)
C(16)	11912(3)	3037(6)	8528(3)	65(1)
Cl(1)	6927(1)	2170(2)	908(1)	82(1)
O(3)	6849(7)	1054(11)	1608(6)	71(3)
O(4)	7855(5)	2459(18)	893(10)	145(6)
O(5)	6655(9)	1338(15)	186(6)	103(4)
O(6)	6480(9)	3554(11)	1083(8)	76(4)

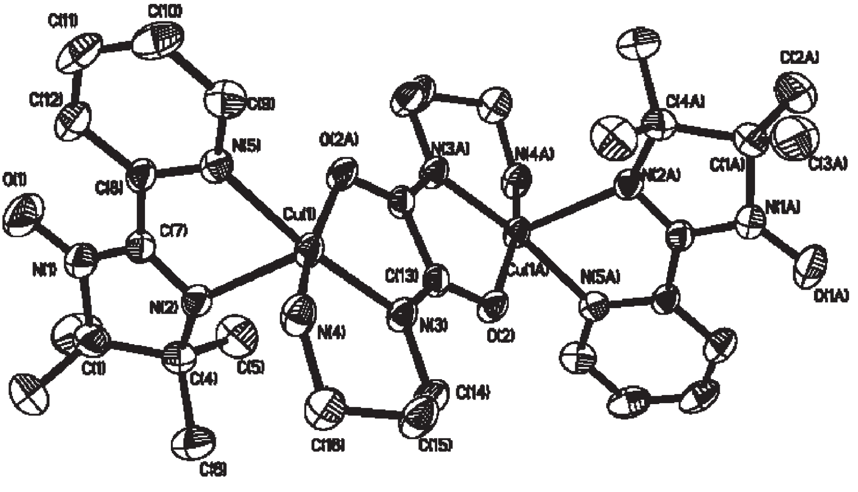


Figure 1. ORTEP view of the $[Cu_2(oxpn)(IM2py)_2]^{2+}$ cation showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% level. H atoms and ClO_4^- ions are omitted for clarity.

forms an angle of 14.1° with the pyridine plane. The separation of the nearest Cu(II) ions through the oxamido bridge is 5.222 Å.

3.2. *IR and electronic spectra*

IR spectra of the complex show two strong bands at approximately 3300 and 1630 $\mathrm{cm^{-1}}$, attributed to $\nu_{\mathrm{N\text{–}H}}$ and $\nu_{\mathrm{C=O}}$ bands of the oxamido ligand, respectively. A medium intensity absorption at 1360 $\mathrm{cm^{-1}}$ attributed to the N–O stretch suggests that the nitrogen atom of the conjugated group (NCNO) of the radical coordinate to the metal ions, in agreement with the results of the crystal structure. A broad strong band at approximately 1080 $\mathrm{cm^{-1}}$ is characteristic of the perchlorate ion. Electronic absorption spectra were measured in DMSO solution. The complex exhibits very intense bands below 400 nm, assignable to charge–transfer transitions between metal ion and ligand, and intra-radical ligand transitions [10–12], respectively. In the 480–630 nm region, the complex exhibits a broad band assigned to spin-allowed d–d transitions of Cu(II) in a distorted square pyramidal environment [13].

3.3. *Magnetic characterization*

The magnetic susceptibility of the complex has been measured in the range 2–300 K. Magnetic exchange can occur either through two Cu(II) ions via the *trans*-oxamido bridge between or Cu(II) and the nitroxide radical ligand. To characterize quantitatively the magnetic behaviour of the complex, the spin Hamiltonian describing the four-spin system can be given as $\hat{\mathrm{H}} = -2J\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Cu2}} - 2J(\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{R1}} + \hat{S}_{\mathrm{Cu2}}\hat{S}_{\mathrm{R2}})$, where J and j stand for the Cu(II)–Cu(II) and Cu(II)-radical magnetic interactions, respectively. Assuming $g_{\mathrm{Cu}} = g_{\mathrm{R}} = g$, the magnetic data were preliminarily analyzed with the equation based on the above isotropic Hamiltonian, with the molar susceptibility being given as

$$\chi = \frac{Ng^2\beta^2}{KT}\frac{A}{B}$$

where $A = 10\exp(-E_1/KT) + 2\exp(-E_2/KT) + 2\exp(-E_3/KT) + 2\exp(-E_4/KT)$, $B = 5\exp(-E_1/KT) + 3[\exp(-E_2/KT) + \exp(-E_3/KT) + \exp(-E_4/KT)] + \exp(-E_5/KT) + \exp(-E_6/KT)$, $E_1 = -j - J/2$, $E_2 = j - J/2$, $E_3 = J/2 + (J^2 + j^2)^{1/2}$, $E_4 = J/2 - (J^2 + j^2)^{1/2}$, $E_5 = j + J/2 + (4j^2 - 2jJ + J^2)^{1/2}$ and $E_6 = j + J/2 - (4j^2 - 2jJ + J^2)^{1/2}$. Variation of χ_{M} and $\chi_{\mathrm{M}}T$ *versus* T is presented in figure 2, where χ_{M} is the molar magnetic susceptibility and T is the absolute temperature. The room temperature value of $\chi_{\mathrm{M}}T$ (1.077 $\mathrm{cm^3\,K\,mol^{-1}}$) is much lower than that expected for four uncorrelated spins with $S = 1/2$ ($\chi_{\mathrm{M}}T = 1.5\ \mathrm{cm^3\,K\,mol^{-1}}$); $\chi_{\mathrm{M}}T$ decreases slowly upon lowering the temperature and gives a plateau around 130 K. The temperature dependence of the magnetic susceptibility of the complex was fitted to the equation to give the best fit values $J = -187.02\ \mathrm{cm^{-1}}$, $j = 30.05\ \mathrm{cm^{-1}}$, $g = 2.06$, and the agreement factor $R = \sum[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{Calcd}}]^2 / \sum(\chi_{\mathrm{M}})^2_{\mathrm{obs}} = 8.68 \times 10^{-4}$. As expected, the magnetic interaction between two Cu(II) ions through the *trans*-oxamide bridge is strongly antiferromagnetic [14]. Ferromagnetic exchange is implied for the interaction between Cu(II) and IM2py. According to the X-ray crystal structure analysis, the nitrogen atom

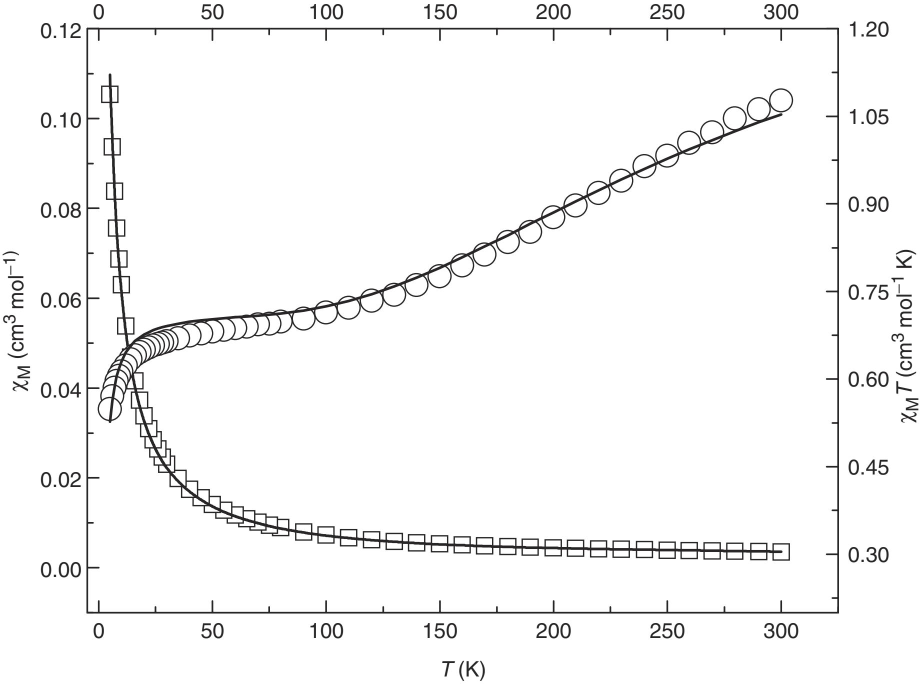


Figure 2. χ_M(□) and $\chi_M T$ (○) *vs*. T plots for the complex. The solid lines represent the best fits of the data with values in the text.

of the nitroxide radical ligand is coordinated to Cu(II) ion at the apex of a square pyramid. In the case, the unpaired electrons of the nitroxide radical delocalize on the π orbital orthogonal to the $d_{x^2-y^2}$ orbital of Cu(II). This results in the ferromagnetic interaction between Cu(II) and the radical, and the value of j should be positive [15].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 260169. 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; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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