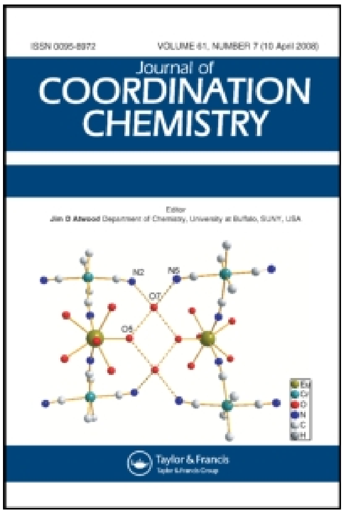

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Structures and magnetic properties of two new heterospin complexes involving nitroxide radicals and oxamido-bridged copper(II)

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Two new binuclear copper(II) complexes containing four spin carriers with pyridyl-substituted nitroxide radicals have been synthesized and characterized structurally and magnetically. These complexes are formulated as $[Cu_2(oxap)(IM4py)_2](ClO_4)_2$ (**1**) and $[Cu_2(oxap)(NIT4py)_2](ClO_4)_2$ (**2**), respectively, in which oxap stands for *N*,*N′*-*bis*(2-aminopropyl). IM4py stands for 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl and NIT4py for 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide. The structures of the complexes consist of centrosymmetric *trans* oxamido-bridged copper(II) binuclear units and nitroxide radicals. In **1** and **2** the copper atoms are in a distorted square plane and radicals (IM4py and NIT4py) coordinate to copper *via* nitrogen atoms from pyridine rings. Magnetic analysis indicates that **1** and **2** exhibit strong metal-metal antiferromagnetic coupling through oxamido-bridged and antiferromagnetic exchange interactions between copper(II) ion and radicals, respectively. The magnetic behaviors are discussed with reference to their crystal structures.

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

1. Introduction

Nitroxide radicals, independently or in combination with metal ions, have been one of the most widely studied systems in molecular magnetism for understanding radical–radical or metal–radical interactions as well as for synthesizing organic ferromagnets and metal–radical magnetic materials [1]. The heterospin systems consisting of organic free radicals and paramagnetic metal ions constitute one of the most promising design strategies for high Curie-temperature molecular-based magnets [2, 3].

Polynuclear complexes are of interest for designing new magnetic materials and for investigating the structures. One strategy to design and synthesize polynuclear species is the ‘complex as ligand’ approach, i.e., the use of mononuclear complexes that contain

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potential donor groups for another metal ion. A good example of 'complex ligands' is represented by the mononuclear Cu(II) complexes of *N*,*N′*-*bis*(coordinating-group)-substituted oxamides [4] such as [Cu(oxpn)] and [Cu(oxap)]. These ligands undergo easy *cis–trans* transformation upon coordination to metal ions, which makes it practical to design tunable molecular materials with extended structures and desired properties [5, 6].

We have designed and synthesized two heterospin complexes, Cu_2(oxap)$(IM4py)_2]$ $(ClO_4)_2$ (**1**) and $[Cu_2$(oxap)$(NIT4py)_2](ClO_4)_2$ (**2**), oxamido-bridged bimetallic complexes involving pyridyl-substituted nitroxide radical ligands, where oxap stands for *N*,*N′*-*bis*(2-aminopropyl) oxamido; IM4py is for 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl and NIT4py for 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide.

2. Experimental

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin–Elmer elemental analyzer. Infrared spectra were taken on a BRUKER TENSOR 27 IR spectrophotometer model 408 in the 4000–400 cm^{-1} region using KBr pellets. Variable temperature susceptibility measurements of crystalline samples were carried out in the temperature range 2–300 K, using a SQUID MPMS XL-7 magnetometer at a magnetic field of 2000 G. Molar susceptibility was corrected from the sample holder and diamagnetic corrections of all constituent atoms by using Pascal's constants.

2.2. *Materials and synthesis*

All chemicals were of analytical grade and used as purchased without further purification. The mononuclear precursor Cu(oxap) was synthesized according to the reported procedure [7]. The pyridyl-substituted radicals IM4py and NIT4py were prepared according to the literature [8, 9].

Complex **1**, $[Cu_2$(oxap)$(IM4py)_2](ClO_4)_2]$, was prepared by the following method: to a green aqueous methanol solution (20 mL in 1 : 1 ratio) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol) and Cu(oxap) (2 mmol) was added (4 mmol) IM4py dissolved in 10 mL of methanol. The mixture was stirred for 2 h at room temperature and filtered. The filtrate was kept at room temperature; within a couple of days well-formed dark-green crystals of $[Cu_2$(oxap)$(IM4py)_2](ClO_4)_2$, suitable for an X-ray structure determination, were obtained. Yield: 62%.

Complex **2**, $[Cu_2$(oxap)$(NIT4py)_2](ClO_4)_2]$, was synthesized in the same way as **1**, except that IM4py was replaced by NIT4py (4 mmol) to give well-formed dark-blue crystals. Yield: 65%.

Elemental analyses (%) Calcd $C_{32}H_{48}Cl_2Cu_2N_{10}O_{12}$ (**1**): C, 39.92; H, 5.02; N, 14.55. Found: C, 39.86; H, 4.91; N, 14.50; Calcd $C_{32}H_{46}Cl_2Cu_2N_{10}O_{14}$ (**2**): C, 38.71; H, 4.67; N, 14.11. Found: C, 38.64; H, 4.81; N, 14.06.

2.3. *X-ray crystallography*

The data collection was carried out on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Determinations of the crystal class, orientation matrix, and cell dimensions were performed according to the established procedures. The intensity data were collected by ϕ–ω scan technique.

The structures were solved with direct methods using SHELXS-97 [10] and refined with full-matrix least-square based on F^2 using SHELXL-97 [11]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. All non-hydrogen atoms were refined anisotropically. Reliability factors were defined as $R_1 = \sum(\|F_o| - |F_c\|)/\sum\|F_o\|$, and the function minimized was $wR_2 = (\sum(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2)^{1/2}$, where in the least squares calculation the unit weight was used. Crystallographic data and details of data collection are listed in table 1. Selected bond distances and angles are listed in table 2 (for **1**) and 3 (for **2**), respectively.

Table 1. Crystallographic data of **1** and **2**.

Complex	**1**	**2**
Formula	$C_{32}H_{48}Cl_2Cu_2N_{10}O_{12}$	$C_{32}H_{46}Cl_2Cu_2N_{10}O_{14}$
Formula weight	962.78	992.77
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	15.494(5)	14.815(13)
b (Å)	11.664(4)	11.814(10)
c (Å)	11.089(3)	12.552(12)
β (°)	99.198(4)	103.811(13)
Z	2	2
Density (ca) (Mg m^{-3})	1.616	1.545
F(000)	996	1024
Crystal size (mm^3)	0.36 × 0.22 × 0.12	0.40 × 0.32 × 0.22
θ range for data collection (°)	2.20–25.02	2.23–25.01
Reflections collected/unique	10,470/3747 [R(int) = 0.0693]	10,512/3478 [R(int) = 0.0185]
Data/restraints/parameters	3478/0/267	3747/0/276
Goodness-of-fit on F^2	1.061	1.090
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$	$R_1 = 0.0664$
R indices (all data)	$wR_2 = 0.0906$	$wR_2 = 0.1590$

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)–N(5)	1.921(2)	N(2)–C(4)	1.485(3)
Cu(1)–N(3)	1.991(2)	N(3)–C(11)	1.331(3)
Cu(1)–O(2)	2.0213(19)	N(3)–C(10)	1.331(3)
Cu(1)–N(4)	2.029(2)	N(4)–C(14)	1.457(4)
O(1)–N(1)	1.270(3)	N(5)–Cu(1)–N(3)	171.45(10)
O(2)–C(16)	1.271(3)	N(5)–Cu(1)–O(2)	82.35(8)
N(1)–C(7)	1.385(3)	N(3)–Cu(1)–O(2)	95.84(8)
N(1)–C(3)	1.492(3)	N(5)–Cu(1)–N(4)	82.24(9)
N(2)–C(7)	1.277(3)	N(3)–Cu(1)–N(4)	99.90(9)

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

3. Results and discussion

3.1. *Crystal structures*

X-ray crystallography reveals that two complexes are isomorphous and isostructural with the previously reported $[Cu_2(oxen)(NITppy)_2]^{2+}$ [12]. Only the nitrogen atoms of the pyridine rings are coordinated to the *trans*-oxamido-bridged copper(II) binuclear unit to form a four-spin complex. The coordination geometry around each Cu(II) ion adopts a distorted square plane, composed of one carbonyl oxygen and three nitrogen atoms from the amide, amine and pyridine groups, respectively. ORTEP drawings of the cations are shown in figures 1 and 2. In **1**, the structure consists of one binuclear centrosymmetric complex cation $[Cu_2(oxap)(IM4py)_2]^{2+}$ and two perchlorate anions. Four atoms around each Cu(II) are displaced by 0.0751 Å (N3) and 0.1037 Å (N5) above and

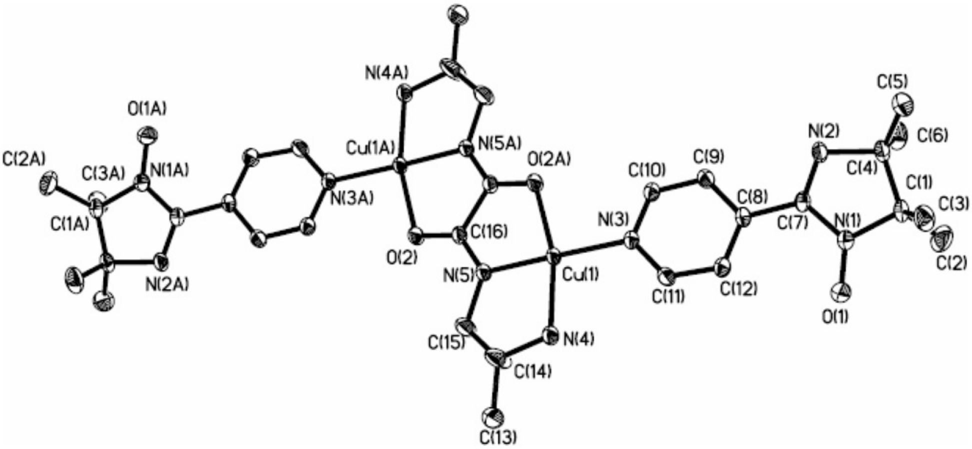

Figure 1. ORTEP view of $[Cu_2(oxap)(IM4py)_2]^{2+}$ of **1** with thermal ellipsoids drawn at 30%. H atoms and ClO_4^- are omitted for clarity.

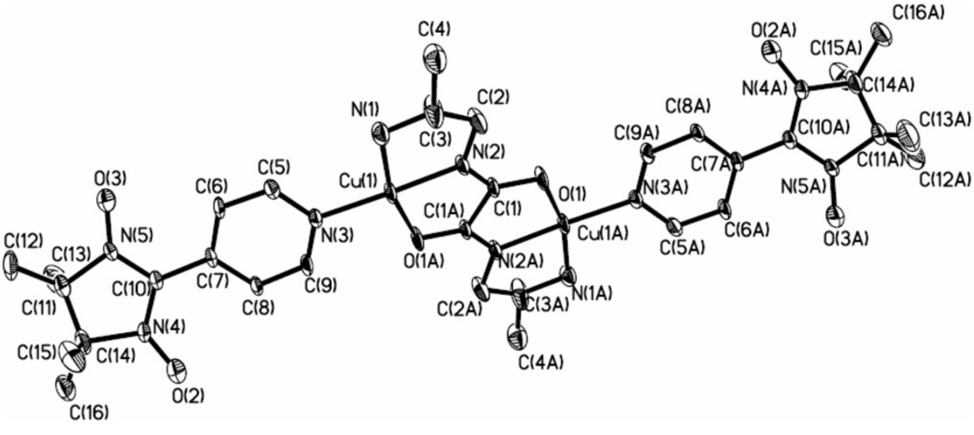

Figure 2. ORTEP view of $[Cu_2(oxap)(NIT4py)_2]^{2+}$ of **2** with thermal ellipsoids drawn at 30%. H atoms and ClO_4^- are omitted for clarity.

0.0880 Å (N4) and 0.0909 Å (O2A) below the mean plane. The deviation of the copper(II) ion from the mean plane is 0.0521 Å. The bond lengths of the Cu(II)–N bonds in **1** are in the range 1.921(2)–2.029(2) Å. The mean plane of the imidazoline ring shows a dihedral angle of 14.9° with the basal plane around Cu(1) and Cu(1A). The imidazoline ring of the nitroxide radical forms an angle of 15.3° with the pyridine plane. The separation of the nearest Cu(II) ions through the oxamido bridge is 5.276 Å.

Similar to **1**, complex **2** consists of one binuclear centrosymmetric cation $[Cu_2(oxap)(NIT4py)_2]^{2+}$ and two perchlorate anions. The bond lengths of the Cu(II)–N bonds in **2** are in the range 1.916(5)–2.023(6) Å. The mean plane of the imidazoline ring shows a dihedral angle of 44.2° with the basal plane around Cu(1) and Cu(1A). The imidazoline ring of the nitroxide radical forms an angle of 24.1° with the pyridine plane. The separation of the nearest Cu(II) ions through the oxamide bridge is 5.227 Å.

3.2. *IR and electron spectra*

The IR spectra of **1** and **2** show two strong bands at approximately $3300\,cm^{-1}$ and $1630\,cm^{-1}$, attributed to $\nu_{(N\text{–}H)}$ and $\nu_{(C=O)}$ stretching bands of the oxamido ligand, respectively. The stretching vibration of the N–O of the radical appears at $1370\,cm^{-1}$, which indicates that the nitrogen atom of the conjugate group (NCNO) of the radicals does not coordinate to copper. A broad strong band at $1080\,cm^{-1}$ is characteristic of perchlorate. These results are in agreement with the crystal structures.

The electronic absorption spectra of **1** and **2** measured in DMSO solutions exhibit very intense bands below 400 nm, assigned to charge-transfer transitions between metal ion and ligand, and intra-radical ligand transitions [13–15], respectively. In the region of 550–700 nm, **1** and **2** exhibit broad bands assigned to the spin allowed d–d transitions of square planar Cu(II) [16].

3.3. *Magnetic characterization and discussion*

The magnetic susceptibilities of the complexes have been measured in the range of 2–300 K. In **1** and **2**, magnetic exchange occurs either between Cu(II) ions through the *trans*-oxamido bridge or Cu(II) ion with nitroxide radical ligands. To characterize quantitatively the magnetic behavior, the spin Hamiltonian describing the situation of these four-spin system can be given as $\hat{H} = -2J\hat{S}_{Cu1}\hat{S}_{Cu2} - 2j(\hat{S}_{Cu1}\hat{S}_{R1} + \hat{S}_{Cu2}\hat{S}_{Cu2})$,

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cu(1)–N(2)	1.916(5)	N(5)–C(11)	1.507(9)
Cu(1)–N(3)	1.993(5)	C(2)–C(3)	1.459(12)
Cu(1)–O(1)	2.001(5)	N(2)–Cu(1)–N(3)	172.5(3)
Cu(1)–N(1)	2.023(6)	N(2)–Cu(1)–O(1)	83.7(2)
O(1)–C(1)	1.278(7)	N(3)–Cu(1)–O(1)	92.3(2)
O(2)–N(4)	1.268(8)	N(2)–Cu(1)–N(1)	82.1(2)
O(3)–N(5)	1.275(8)	N(3)–Cu(1)–N(1)	101.6(2)
N(1)–C(3)	1.446(10)	O(1)–Cu(1)–N(1)	165.7(2)
N(2)–C(1)	1.286(8)	C(1)–O(1)–Cu(1)	109.4(4)
N(2)–C(2)	1.453(9)	C(3)–N(1)–Cu(1)	111.4(5)

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

where J and j stand for Cu(II)–Cu(II) and Cu(II)–Rad magnetic interactions [12], respectively. Assuming $g_{\mathrm{Cu}} = g_{\mathrm{R}} = g$ and the magnetic data analyzed with the magnetic equation based on the above isotropic Hamiltonian, the expression of the mole susceptibility can be given as:

$$\chi = \frac{\mathrm{N}g^2\beta^2}{KT}\frac{\mathrm{A}}{\mathrm{B}} \tag{1}$$

$$\begin{aligned}
A &= 10\exp(-E_1/KT) + 2\exp(-E_2/KT) + 2\exp(-E_3/KT) + 2\exp(-E_4/KT)\\
B &= 5\exp(-E_1/KT) + 3[\exp(-E_2/KT) + \exp(-E_3/KT)\\
&\quad + \exp(-E_4/KT)] + \exp(-E_5/KT) + \exp(-E_6/KT)\\
E_1 &= -j - J/2\\
E_2 &= j - J/2\\
E_3 &= J/2 + (J^2 + j^2)^{1/2}\\
E_4 &= J/2 - (J^2 + j^2)^{1/2}\\
E_5 &= j + J/2 + (4j^2 - 2Jj + J^2)^{1/2}\\
E_6 &= j + J/2 - (4j^2 - 2jJ + J^2)^{1/2}
\end{aligned}$$

The variation of χ_{M} and $\chi_{\mathrm{M}}T$ *versus* T for **1** is represented in figure 3. The value of $\chi_{\mathrm{M}}T$ at room temperature is $1.13\,\mathrm{cm^3\,K\,mol^{-1}}$, which is much lower than expected for four uncorrelated spins with $S = 1/2$ ($\chi_{\mathrm{M}}T = 1.5\,\mathrm{cm^3\,K\,mol^{-1}}$), and further decreases on

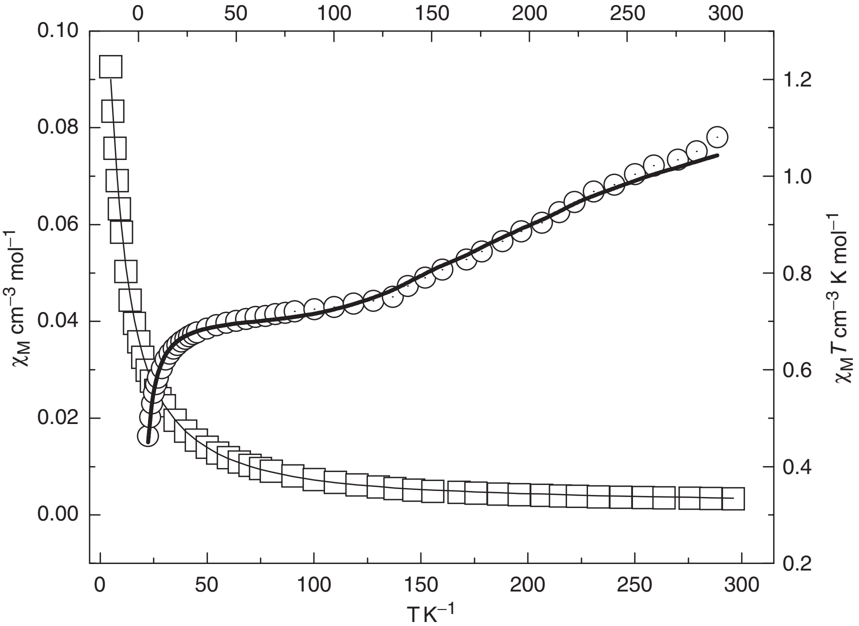

Figure 3. The χ_{m}(□) and $\chi_{\mathrm{m}}T$ (⊙) *vs.* T plots of **1**. The solid lines represent the best fit of the data with values in the text.

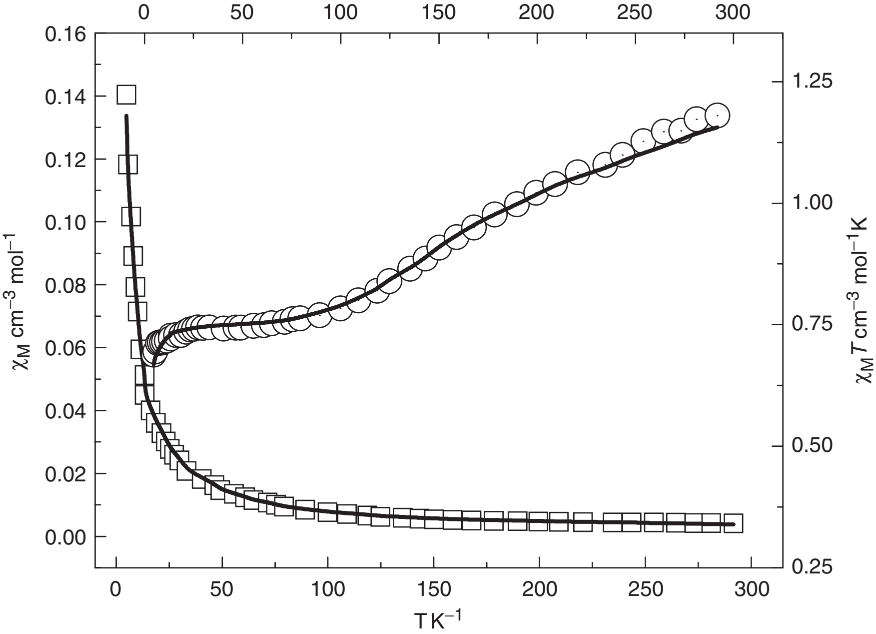

Figure 4. The χ_m(□) and $\chi_m T$ (⊙) *vs.* T plots of **2**. The solid lines represent the best fit of the data with values in the text.

lowering the temperature. This implies strong anti-ferromagnetic interaction in this compound. According to equation (1), the best fitting leads to $J = -186.97\,\text{cm}^{-1}$, $j = -26.98\,\text{cm}^{-1}$, $g = 2.06$, and the agreement factor $R = \sum[(\chi_M)_{obs} - (\chi_M)_{Calcd}]^2/\sum \chi_M)^2_{obs} = 2.81 \times 10^{-4}$. The results for **2** are similar to **1**. The variation of χ_M and $\chi_M T$ *versus* T is represented in figure 4. According to equation (1), $J = -176.62\,\text{cm}^{-1}$, $j = -19.71\,\text{cm}^{-1}$, $g = 2.06$, and the agreement factor $R = \sum[(\chi_M)_{obs} - (\chi_M)_{Calcd}]^2/\sum(\chi_M)^2_{obs} = 3.18 \times 10^{-4}$.

The results indicate strong anti-ferromagnetic interaction between copper(II) ions through the oxamido-bridge, due to good overlap of the magnetic orbital of both copper(II) ions and the J_{Cu-Cu} value is comparable to data reported for other oxamido-bridged copper(II) complexes [17–19]. The magnetic interaction between Cu(II) and nitroxide radical ligands through the pyridine ring is weakly anti-ferromagnetic [20]. This is in agreement with the following: (1) the nitrogen atom of the pyridine ring lies on the basal plane of the Cu(II) and (2) according to the spin polarization mechanism, the nitrogen atom of the pyridine ring has small spin density.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, deposition numbers: CCDC-260170 for **1** and CCDC-281074 for **2**, respectively. 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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