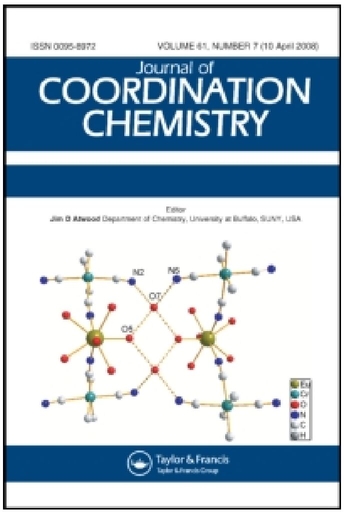

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Copper(I) halide complexes with a sterically hindered thiourea: synthesis and crystal structures of [Cu(dchtu)$_2$Cl] and [Cu(dchtu)$_2$Br] (dchtu = *N*,*N*′-dicyclohexylthiourea)

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Copper(I) complexes with a sterically hindered thiourea, [Cu(dchtu)$_2$X] (dchtu = *N*, *N*′-dicyclohexylthiourea; X=Cl **1**, Br **2**), were synthesized and their crystal structures were determined. Compounds **1** and **2** are isostructural orthorhombic, space group $P2_12_12_1$. Crystallographic data for **1**: $a = 13.1711(13)$, $b = 14.2610(19)$, $c = 15.793(2)$ Å, $V = 2966.4(6)$ Å^3, $Z = 4$. For **2**: $a = 13.2628(13)$, $b = 14.3410(19)$, $c = 15.860(2)$ Å, $V = 3016.5(6)$ Å^3, $Z = 4$. The stoichiometry of CuX complexes with thiourea is influenced by substituents on the nitrogens. Copper(I) halides only form bis-adducts with the sterically hindered dchtu ligand even with molar excesses of dchtu due to steric hinderance of the cyclohexyl substituents. In **1** and **2**, the Cu(I) is trigonally coordinated by the sulfur atoms of two monodentate *N*,*N*′-dicyclohexylthiourea ligands and one halide. The structures of the complexes are stabilized by a system of intermolecular H-bonding.

Keywords: Synthesis; Crystal structure; Copper(I) complex; *N*,*N*′-dicyclohexylthiourea

1. Introduction

Metal complexes of thiourea are used as starting materials in chemical spray pyrolysis (CSP) processes used to prepare thin films or sheets of binary or ternary sulfides [1, 2]. Metal sulfides have potential applications such as conductive electrodes [3], solar cells [4], superionic materials [5], recognition of metal ions [6, 7] and biological applications [8–10]. The widely used CSP processes are usually prepared by dissolving Cu(I) salts with thiourea in solution or adding thiourea to solutions of Cu(II) salts, resulting in reduction of Cu(II) to Cu(I) [11–14]. Copper(I) thiourea complexes crystallize with various compositions according to the thiourea/copper molar ratio, the type of copper salt and the solvent used in the preparation [15–25]. Besides the molar ratio of reactants in the precursor solution, the substituents on nitrogen of thiourea might have a significant influence on the compositions and structures of the resulting thin film. Therefore, studies on the syntheses and structural characterization of copper(I) complexes with substituted thiourea derivatives contribute to a better understanding

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and design of spray pyrolysis processes for the copper and sulfur containing thin films or sheets.

The chemical properties of thiourea are readily modified by substituents on nitrogen. *N*,*N*′-dicyclohexylthiourea (dchtu) is a thiourea derivative with bulky substituents. Toshimi *et al*. found that plates or sheets prepared by a mixture of sterically bulky *N*,*N*′-dicyclohexylthiourea (dchtu) and copper acetylacetonate is capable of absorbing near IR-rays, providing superior optical materials for shielding sunlight thermic rays [26]. However, the composition and structure of the copper complex are not known. The only example of dchtu complexes with metals is a tellurium(II) compound [Te(dchtu)$_2$Cl]Cl [27]. Herein we report copper(I) complexes [Cu(dchtu)$_2$Cl] and [Cu(dchtu)$_2$Br] by reactions of copper(II) halides with dchtu. The present contribution reports the synthesis and crystal structures of the new copper(I) complexes.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were commercial materials of analytical grade and used without further purification. FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. C, H and N analysis was measured on a MOD 1106 elemental analyzer. Thermoanalysis was performed using a TGA-DSC microanalyzer of SDT 2960 and all the samples were heated under a nitrogen stream of $100\,\mathrm{mL\,min^{-1}}$ with a heating rate of $5^\circ\mathrm{C\,min^{-1}}$. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a UNITY INOVA 400 MHz NMR spectrometer with TMS as internal standard.

2.2. *Syntheses of the complexes*

2.2.1. Synthesis of [Cu(dchtu)$_2$Cl] (1). To a solution of dchtu (215 mg, 0.894 mmol) in C_2H_5OH (10 mL) was added a solution of $CuCl_2$ (40 mg, 0.298 mmol) in C_2H_5OH (3 mL). After the resulting mixture was stirred at room temperature for 30 min, a clear colorless solution was obtained. Slow evaporation of the solution at room temperature formed colorless block crystals of **1** in 68% yield (117 mg) based on $CuCl_2$. **1** is soluble in common organic solvents, such as C_2H_5OH, CH_3CN, and $CHCl_3$. Anal. Calcd for $C_{26}H_{48}N_4S_2ClCu$ (%): C, 53.86; H, 8.34; N, 9.66. Found: C, 53.77; H, 8.31; N, 9.54. IR data (KBr pellets, cm^{-1}): 3119w (νN–H), 1145s (νC=S), 1521 *versus* (νC–N). ^{1}H NMR (δ): 7.51 (m, 4H, NH), 2.99–2.97 (s, 4H, NCH), 1.76–1.20 (s, 40H, C_5H_{10}).

2.2.2. Synthesis of [Cu(dchtu)$_2$Br] (2). To a solution of dchtu (219 mg, 0.912 mmol) in C_2H_5OH (10 mL) was added a solution of $CuBr_2$ (68 mg, 0.304 mmol) in C_2H_5OH (3 mL). A clear colorless solution was formed after the resulting mixture was stirred at room temperature for 30 min. Slow evaporation of the solution at room temperature formed colorless block crystals of **2** in 76% yield (144 mg) based on $CuBr_2$. The solubility of **2** is similar to that of **1**. Anal. Calcd for $C_{26}H_{48}N_4S_2BrCu$ (%): C, 50.02; H, 7.75; N, 8.97. Found: C, 49.88; H, 7.68; N, 8.82. IR data

(KBr pellets, cm^{-1}): 3098w (νN–H), 1141s (νC=S), 1518vs (νC–N). ^{1}H NMR (δ): 7.45 (m, 4H, NH), 3.01–2.98 (s, 4H, NCH), 1.74–1.18 (s, 40H, C_5H_{10}).

2.3. *Crystal structure determination*

Data were collected on a Rigaku Mercury CCD diffractometer at 193(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) in a ω-scanning mode in the range $6.02 \le 2\theta \le 50.70$ for **1** and $6.14 \le 2\theta \le 50.68$ for **2**. An absorption correction was applied for all data with multi-scan. The structures were solved with direct methods using SHELXS-97 [28] and structure refinements were done against F^2 with SHELXL-97 [29]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. Technical details of data acquisition and selected refinement results are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and IR spectral studies*

Reactions of copper(II) salts $CuCl_2$ and $CuBr_2$ with dchtu in C_2H_5OH form exclusively 1 : 2 stoichiometric Cu(I) complexes **1** and **2**, respectively. The reduction of Cu(II) to

Table 1. Crystal data and structure refinement details for **1** and **2**.

CCDC deposit no.	CCDC–641132	CCDC–641133
Formula	$C_{26}H_{48}N_4S_2ClCu$	$C_{26}H_{48}N_4S_2BrCu$
Formula weight	579.79	624.25
Color, habit	Colorless, block	Colorless, block
Dimensions (mm^3)	$0.24 \times 0.19 \times 0.11$	$0.27 \times 0.22 \times 0.21$
T (K)	193(2)	193(2)
λ (Mo-Kα) (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å)	13.1711(13)	13.2628(13)
b (Å)	14.2610(19)	14.3410(19)
c (Å)	15.793(2)	15.860(2)
V (Å^3)	2966.4(6)	3016.5(6)
Z	4	4
D_{calcd} ($g\,cm^{-3}$)	1.298	1.375
F(000)	1240	1312
Absorption coefficient (mm^{-1})	0.988	2.208
θ range for data collection (°)	$3.01 \le \theta \le 25.35$	$3.07 \le \theta \le 25.34$
Index ranges	$-15 \le h \le 14$ $-17 \le k \le 17$ $-19 \le l \le 16$	$-15 \le h \le 14$ $-17 \le k \le 17$ $-17 \le l \le 19$
Reflections collected	29859	30246
Independent reflections	5420 ($R_{int} = 0.0737$)	5498 ($R_{int} = 0.0445$)
Reflections with $[I > 2\sigma(I)]$	4732	5200
Parameters	324	324
Goodness of fit on F^2	1.105	1.123
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0485$, $wR_2 = 0.0873$	$R_1 = 0.0319$, $wR_2 = 0.0351$
R indices (all data)	$R_1 = 0.0595$, $wR_2 = 0.0910$	$R_1 = 0.0574$, $wR_2 = 0.0586$
Largest diff. peak and hole (e Å^{-3})	−0.283 and 0.301	−0.237 and 0.304

Cu(I) by thiourea and its derivatives is common and a number of copper(I) complexes have been obtained from copper(II) salts by *in situ* reduction in the presence of thiourea or its derivatives [21–25, 30–34]. Using three or four-fold molar excesses of dchtu in the reactions also gives rise to bis-adducts of dchtu. In contrast, the stoichiometry of Cu(I) halide complexes with thiourea depends on the ratio between Cu(I) and thiourea (tu) in solution, $[Cu(tu)]X \cdot 0.5H_2O$ [15], $[Cu(tu)_2Cl]$ [18, 19], and $[Cu(tu)_3]X$ (X=Cl, Br) [15, 20]. The sterically hindered nature of dchtu limits substitution despite the molar excess of dchtu.

IR spectra of the complexes showed characteristic peaks due to *N*,*N*′-dicyclohexylthiourea and some important ones are listed in section 2. The presence of a ν (N–H) in the region 3098–3119 cm^{-1} as a weak peak shows that the ligand is not deprotonated in the complexes. Broad bands with low intensity could arise from hydrogen-bonded NH. The signal of the C(S)NH proton is present in ^1H NMR spectra showing the existence of the NH proton. A strong ν (C=S) peak at 1153 cm^{-1} in the free ligand shifts to lower range, 1141–1145 cm^{-1}, indicating that the ligand coordinates to the metal via its sulfur; the magnitude of the coordination shift is similar to that reported [15, 23].

3.2. *Crystal structures*

Compounds **1** and **2** crystallize in the orthorhombic space group $P2_12_12_1$ (no. 19) with four formula units in the unit cell and are isostructural. The *N*,*N*′-dicyclohexylthiourea ligand coordinates to Cu(I) center through its sulfur as a monodentate ligand. The structure of compound **1** is depicted in figure 1 and selected bond distances and angles are listed in table 2. The Cu(I) is three-coordinate with sulfur of two different *N*,*N*′-dicyclohexylthiourea ligands and by one chloride forming a trigonal-planar environment. The bond angles around Cu(I) range from 114.53(5) to 126.91(4)° for **1** and from 111.37(11) to 126.41(3)° for **2** (table 2). In **1**, the coordination plane CuS_2Cl is nearly coplanar with the $N_2C(1)S$ skeletal atoms. The torsion angles Cl(1)Cu(1)S(1)C(1) and S(2)Cu(1)S(1)C(1) are 3.46(16)° and −175.44(14)°, respectively. The $N_2C(14)S$ skeletal atoms of the other ligand are not coplanar with the coordination plane CuS_2Cl, indicating steric strain within the complex. The molecular configuration

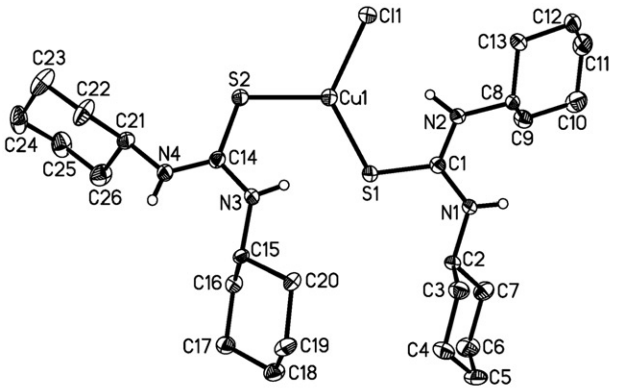

Figure 1. Crystal structure of **1** with the labelling scheme (30% probability ellipsoids). Hydrogen atoms of C-H are omitted for clarity.

of **2** is similar to that of **1**. The Cu–S bond distances (2.2112(12) and 2.2252(12) Å for **1**, 2.2057(9) and 2.2237(9) Å for **2**) (table 2) are similar to those observed in trigonal Cu(I) complexes with *N*,*N*′-dialkyl substituted thioureas, such as 2.2007(7) and 2.2057(6) Å for [CuL$_2$Cl] (L = *N*-ferrocenoyl-*N*′-aryl (alkyl) thiourea [34] and 2.2095(13) and 2.2098(13) Å for [CuL$_2$Cl] (L = *N*-ethoxycarbonyl-*N*′-(*p*-methoxyphenyl)thiourea [35]. The Cu–S bond distances are, as expected, shorter than those of tetrahedral Cu(I)-thiourea complexes, such as 2.2882(7)−2.3853(6) Å for Cu–S in [Cu$_2$(tu)$_6$](SO$_4$)·H$_2$O [22]. The bond lengths, 2.2499(11) Å for Cu−Cl and 2.3801(5) Å for Cu−Br, are consistent with those in the other copper-thiourea derivatives [34–36].

The *N*,*N*′-dialkyl thiourea with coplanar N$_2$CS skeletal atoms can take *trans–trans*, *cis–trans*, and *cis–cis* conformations. *N*,*N*′-dimethylthiourea and *N*,*N*′-diethylthiourea were *trans–trans* isomers in the solid state [37]. In **1** and **2**, *N*,*N*′-dicyclohexylthiourea is *cis–trans* conformation (figure 1). This difference might be related to the steric hinderance of the cyclohexyl substituents and the H-bonding in the complex. In **1** and **2**, hydrogen bonding interactions are formed between thioamide (>N–H) groups and halide ions. In **1**, the N(1)H and Cl(1) of a neighboring molecule form a N–H ··· Cl hydrogen bond [N(1) ··· Cl(1) = 3.531(4) Å], so each [Cu(dchtu)$_2$Cl] forms two equivalent N–H ··· Cl hydrogen bonds with two neighbors. The [Cu(dchtu)$_2$Cl] molecules are arranged in a zigzag chain via those N–H ··· Cl hydrogen bonds (figure 2). The chains are further connected by hydrogen bonds between N(4)H and Cl(1#) [N(4) ··· Cl(1#) = 3.471(4) Å] resulting in a hydrogen-bonded 3D coordination network (figure 3). Similar H-bonding is observed in **2**. The hydrogen bond distances and angles of **1** and **2** are listed in table 3.

The effects of monodentate thione-sulfur coordination are reflected in the thioamide dimensions of ligand. An average lengthening of the C–S distance and an average shortening of the N–C(=S) are observed. On average, the carbon–sulfur (thione) distance is increased from 1.7013(15) Å [38] in the free ligand to 1.721(4) and 1.722(3) Å in **1** and **2**, respectively, while the thioamide carbon-nitrogen distance is correspondingly decreased from 1.338(2) Å [38] in the free ligand to 1.331(4) in **1** and 1.329(4) Å in **2**. The carbon-sulfur and carbon-nitrogen bonds lie between single and double bonds, attributed to delocalization of electron in the amide bond. This extent of the

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

	1	**2**		**1**	**2**
Cu(1)–Cl(1)	2.2499(11)	2.3801(5)	Cu(1)–S(1)	2.2112(12)	2.2057(9)
Cu(1)–S(2)	2.2252(12)	2.2237(9)	S(1)–C(1)	1.724(4)	1.723(3)
S(2)–C(14)	1.717(4)	1.721(3)	N(1)–C(1)	1.324(5)	1.331(4)
N(1)–C(2)	1.475(5)	1.478(4)	N(2)–C(1)	1.337(5)	1.327(4)
N(2)–C(8)	1.468(5)	1.468(4)	N(3)–C(14)	1.346(5)	1.326(4)
N(3)–C(15)	1.469(5)	1.465(4)	N(4)–C(14)	1.328(5)	1.338(4)
N(4)–C(21)	1.469(5)	1.465(4)			
S(1)–Cu(1)–S(2)	118.55(4)	120.42(3)	Cl(1)–Cu(1)–S(1)	126.91(4)	126.41(3)
Cl(1)–Cu(1)–S(2)	114.53(5)	113.13(3)	Cu(1)–S(1)–C(1)	110.66(14)	111.37(11)
Cu(1)–S(2)–C(14)	109.73(14)	108.62(11)			
Cl–Cu(1)–S(1)–C(1)	3.46(16)	0.79(12)	Cl–Cu(1)–S(2)–C(14)	−153.43(15)	−151.14(11)
S(1)–Cu(1)–S(2)–C(14)	25.61(16)	26.70(12)	S(2)–Cu(1)–S(1)–C(1)	−175.44(14)	−176.74(11)
Cu(1)–S(1)–C(1)–N(1)	169.5(3)	12.1(3)	Cu(1)–S(2)–C(14)–N(3)	14.2(4)	−168.9(2)
Cu(1)–S(1)–C(1)–N(2)	13.1(3)	170.3(2)	Cu(1)–S(2)–C(14)–N(4)	−169.2(3)	13.5(3)

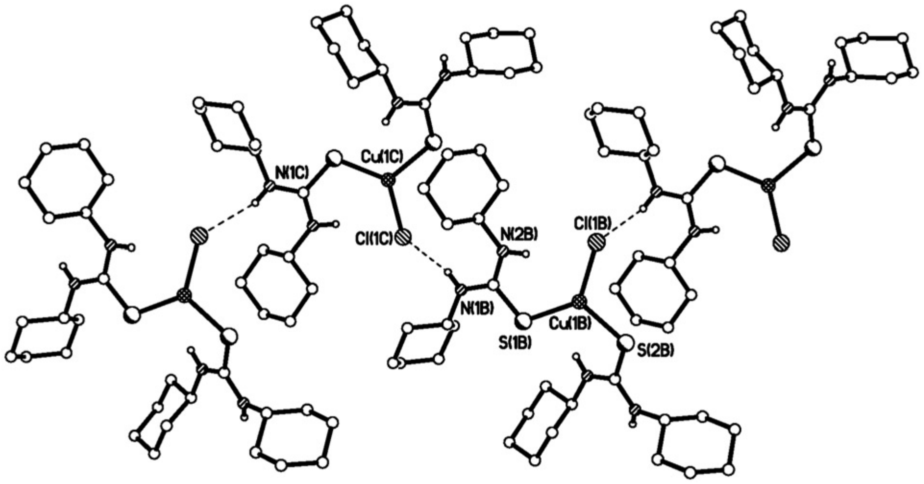

Figure 2. A section packing of [Cu(dchtu)$_2$Cl] molecules in **1** showing the hydrogen bonds.

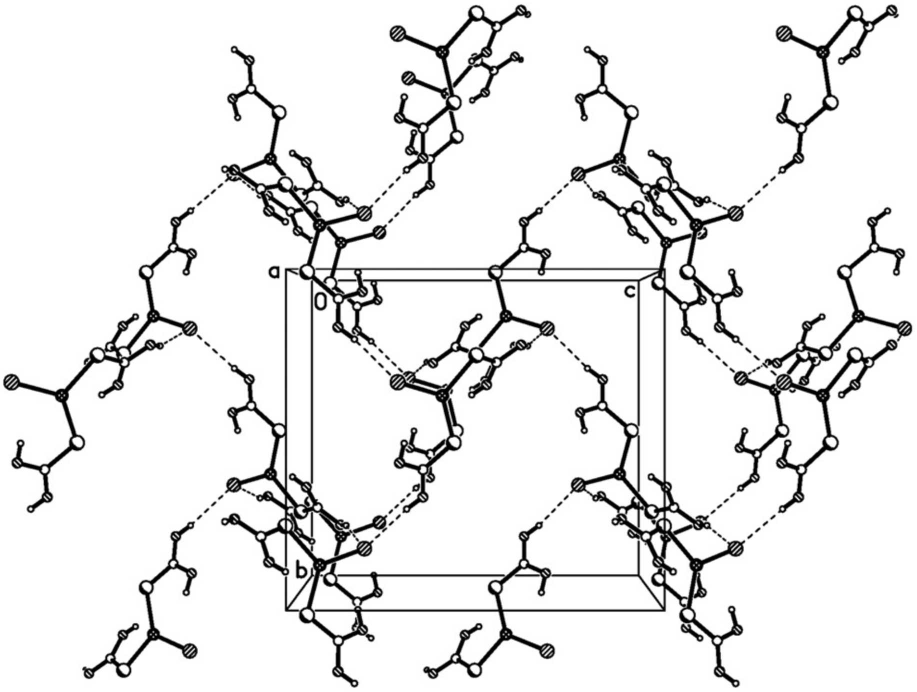

Figure 3. View of the packing of [Cu(dchtu)$_2$Cl] molecules showing the hydrogen bond interactions viewing along the *a* axis. The cyclohexyl rings are omitted for clarity.

dimensional changes is consistent with monodentate thione-sulfur coordination of substituted thiourea ligands [39–41].

Besides forming monomeric complex [Cu(tu)$_4$]$_2$[SiF$_6$] [17] with thiourea, Cu(I) also forms dimeric complexes [Cu$_2$(tu)$_6$]X$_2 \cdot$ 2H$_2$O [21], [Cu$_2$(tu)$_5$]SO$_4 \cdot$ 3H$_2$O [21], and [Cu$_2$(tu)$_6$]SO$_4 \cdot$ H$_2$O [22], tetrameric complexes [Cu$_4$(tu)$_7$](SO$_4$)$_2 \cdot$ H$_2$O [22, 23],

Table 3. List of hydrogen bonds in **1** and **2**.

Atoms in hydrogen bond	H-bond distance (Å)	H-bond angle (°)	Symmetry operator
1			
N(1)–H(1)···Cl(1)	3.531(4)	161(3)	$-x+1, y-1/2, -z+3/2$
N(4)–H(4)···Cl(1)	3.471(4)	166(4)	$x-1/2, -y+1/2, -z+1$
2			
N(1)–H(1)···Br(1)	3.520(3)	171(3)	
N(2)–H(2)···Br(1)	3.572(3)	153(3)	$-x+1, y+1/2, -z+1/2$
N(3)–H(3)···Br(1)	3.557(3)	157(3)	$x-1/2, -y+1/2, -z+1$

$[Cu_4(tu)_6](SO_4)_2 \cdot 2H_2O$ [24], and polymeric complexes $[Cu_8(tu)_{15}](SO_4)_4$ [25] and $[Cu(tu)_3]X$ (X=Cl, Br) [15]. In those polynuclear complexes, thiourea is a bridging ligand to link the Cu(I) centers. It is unlikely for dchtu to act as a bridging ligand because of the steric hinderance of the cyclohexyl substituents, so only monomeric Cu(I) complexes of dchtu are obtained.

Supplementary material

Crystallographic data for the structures reported in the paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary data, CCDC No. 641132 and 641133. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033 or Email: deposit@ccdc.cam.ac.uk).

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