

Crystal structure of a solvated dinuclear Cu^{II} complex derived from 3,3,3',3'-tetraethyl-1,1'-(furan-2,5-dicarbonyl)bis(thiourea)

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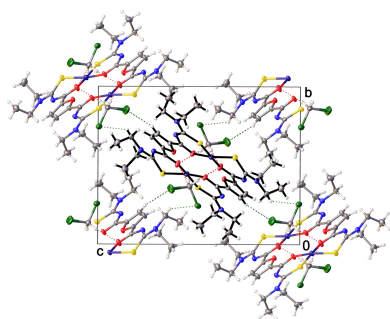
Keywords: crystal structure; aroylbis(*N,N*-dialkylthioureas); Cu(II) complexes.**CCDC reference:** 2400458**Supporting information:** this article has supporting information at journals.iucr.org/e

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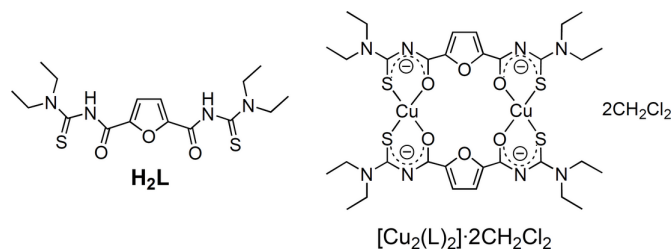
Reaction between equimolar amounts of 3,3,3',3'-tetraethyl-1,1'-(furan-2,5-dicarbonyl)bis(thiourea) (**H₂L**) and CuCl₂·2H₂O in methanol in the presence of the supporting base Et₃N gave rise to a neutral dinuclear complex bis[μ-3,3,3',3'-tetraethyl-1,1'-(furan-2,5-dicarbonyl)bis(thioureaato)]dicopper(II) dichloromethane disolvate, [Cu₂(C₁₆H₂₂N₄O₃S₂)₂·2CH₂Cl₂ or [Cu₂(L)₂·2CH₂Cl₂. The aroylbis(thioureas) are doubly deprotonated and the resulting anions {L²⁻} bond to metal ions through (*S,O*)-chelating moieties. The copper atoms adopt a virtually *cis*-square-planar environment. In the crystal, adjacent [Cu₂(L)₂·2CH₂Cl₂ units are linked into polymeric chains along the *a*-axis direction by intermolecular coordinative Cu···S interactions. The co-crystallized solvent molecules play a vital role in the crystal packing. In particular, weak C—H_{furan}···Cl and C—H_{ethyl}···Cl contacts consolidate the three-dimensional supramolecular architecture.

1. Chemical context

Benzoyl(*N,N*-dialkylthioureas) are versatile ligands forming stable complexes with a great number of transition-metal ions, in which the organic compounds mainly act as monoanionic and (*S,O*)-bidentate ligands (Fitzl *et al.*, 1977; Knuuttila *et al.*, 1982; Sieler *et al.*, 1990; Bensch *et al.*, 1995; Nguyen *et al.*, 2007; Barnard *et al.*, 2019; Pham *et al.*, 2021). This coordination fashion also plays an important role in metal complexes of aroylbis(thioureas), such as homo-dinuclear complexes based on the bipodal *iso*-phthaloylbis(*N,N*-dialkylthioureas) (Koch *et al.*, 2001; Rodenstein *et al.*, 2008; Schwade *et al.*, 2013; Schwade *et al.*, 2020; Teixeira *et al.*, 2020). The presence of potential donor atom(s) in the spacer between two aroylthiourea moieties, such as pyridine N or catechol O atoms, could enable the corresponding aroylbis(thioureas) to serve as building blocks for the construction of heteronuclear host-guest systems (Nguyen *et al.*, 2016; Pham *et al.*, 2017, 2020; Le *et al.*, 2019; Jesudas *et al.*, 2020). However, it seems such aroylbis(thioureas) are not appropriate for the production of homonuclear systems. Indeed, all efforts to produce related homonuclear complexes, as in the case of *iso*-phthaloylbis(*N,N*-dialkylthioureas), have hitherto failed. Herein, we describe the synthesis and crystal structure of the first homonuclear complex derived from the novel 3,3,3',3'-tetraethyl-1,1'-(furan-2,5-dicarbonyl)bis(thiourea) (**H₂L**), referred to as furan-2,5-dicarbonylbis(*N,N*-diethylthiourea), which possesses a potential furan O donor atom in the molecular backbone. The compound, [Cu₂(L)₂], potentially exhibits



interesting magnetic and catalytic properties (Pham *et al.*, 2019; Nath *et al.*, 2020).



2. Structural commentary

The complex $[\text{Cu}_2(\text{L})_2]$ crystallizes as a solvated form in the centrosymmetric monoclinic space group $P2_1/n$ with half of $[\text{Cu}_2(\text{L})_2] \cdot 2\text{CH}_2\text{Cl}_2$ in the asymmetric unit. The molecular structure, including solvent molecules, is shown in Fig. 1. The complex consists of two Cu^{II} ions and two doubly deprotonated ligands $[\text{L}]^{2-}$, which bond to the metal ions through (S,

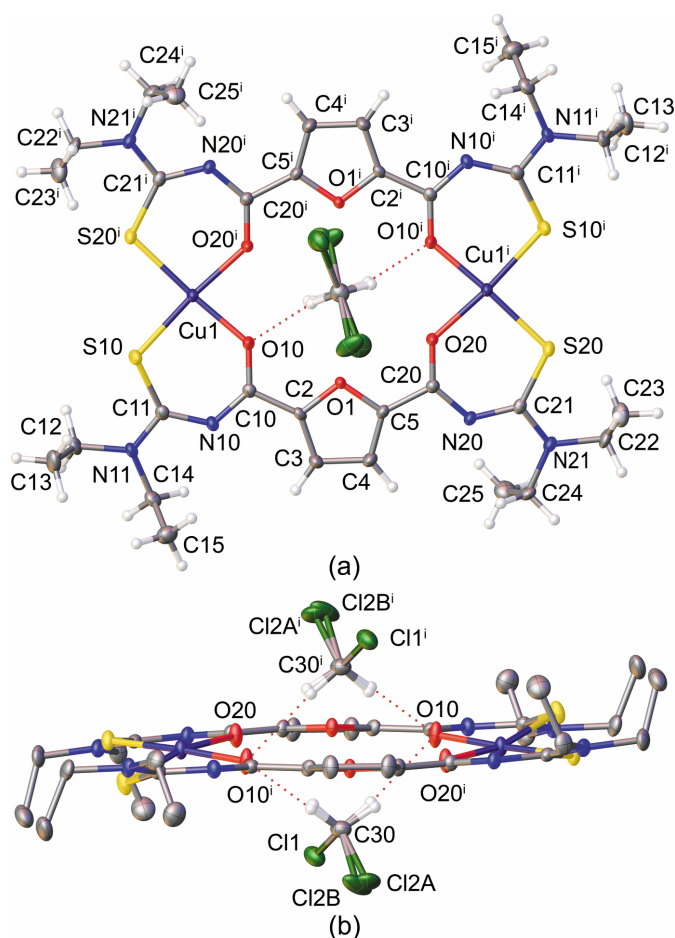


Figure 1
The molecular structure of the title compound $[\text{Cu}_2(\text{L})_2] \cdot 2\text{CH}_2\text{Cl}_2$. (a) Top view with complete labeling of non-hydrogen atoms within the complex molecule. (b) Side view. Hydrogen atoms of the complex are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. The red dotted lines indicate the C—H...O hydrogen bonds. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C}30-\text{H}30\text{A} \cdots \text{O}10$	0.99	2.41	3.388 (3)	171
$\text{C}30-\text{H}30\text{B} \cdots \text{O}10^{\text{i}}$	0.99	2.45	3.428 (3)	171
$\text{C}14-\text{H}14\text{B} \cdots \text{Cl}1^{\text{ii}}$	0.99	2.83	3.627 (2)	138
$\text{C}4-\text{H}4 \cdots \text{Cl}2\text{A}^{\text{iii}}$	0.95	2.68	3.506 (8)	145
$\text{C}4-\text{H}4 \cdots \text{Cl}2\text{B}^{\text{iii}}$	0.95	2.60	3.446 (12)	149

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

O)-chelating aroylthiourea moieties. The $\text{Cu}1-\text{O}$ bond lengths are $\text{Cu}1-\text{O}10 = 1.9406 (15) \text{\AA}$ and $\text{Cu}1-\text{O}20 = 1.9431 (14) \text{\AA}$, while the $\text{Cu}1-\text{S}10$ and $\text{Cu}1-\text{S}20$ bond lengths are $2.2624 (6)$ and $2.2612 (6) \text{\AA}$, respectively. These bond distances fall in the same ranges for those observed in several copper(II) complexes with aroylmono(thioureas) (Wu *et al.*, 2015; Selvakumaran *et al.*, 2016; Binzet *et al.*, 2018; Pham *et al.*, 2021) and aroylbis(thioureas) (Rodenstein *et al.*, 2008; Schwade *et al.*, 2013; Teixeira *et al.*, 2020). The metal...metal distance is $7.762 (3) \text{\AA}$ and the midpoint between the two copper atoms is on the inversion center of the molecule. The two chelate planes $\text{Cu}1/\text{O}10-\text{S}10$ (r.m.s.d. = 0.075\AA) and $\text{Cu}1/\text{O}20-\text{S}10^{\text{i}}$ (r.m.s.d. = 0.156\AA) form a dihedral angle of $15.32 (2)^\circ$. Thus, the four-coordinate Cu^{II} atoms adopt a flat isosceles trapezoid geometry due to the *cis* arrangement of the donor atoms. The atoms within the furan-2,5-dicarboxamide moieties and the copper atoms are nearly coplanar with a largest deviation of $0.298 (2) \text{\AA}$ from the mean least-squares plane for the furan oxygen atoms. Two CH_2Cl_2 molecules are located on either side of the plane at a distance of $1.991 (5) \text{\AA}$ from the plane to the solvent carbon atoms. One chlorine atom of the solvent molecule is disordered over two positions with occupancy factor of $0.6163 (9)$ for the atom labelled A. In addition, the solvent interacts with the complex through hydrogen bonds formed with the carbonyl oxygen atoms $\text{O}10$ (Table 1).

3. Supramolecular features

Each $[\text{Cu}_2(\text{L})_2] \cdot 2\text{CH}_2\text{Cl}_2$ unit interacts with two adjacent ones by long bonding interactions between the Cu^{II} ions and $\text{S}20$ atoms of adjacent blocks (Fig. 2a). These bonds, with a distance of $2.9884 (6) \text{\AA}$, are considerably longer than the coordinative $\text{Cu}-\text{S}$ bonds within the $[\text{Cu}_2(\text{L})_2]$ unit. Such interactions between the units results in polymeric chains along the *a*-axis direction (Fig. 2b).

Furthermore, intermolecular hydrogen bonds (Table 1) involving the solvent molecules and the C—H bonds of the furan rings and ethyl groups are responsible for aggregation of the polymeric chains (Fig. 3).

4. Database survey

The crystal structures of neither the ligand nor its metal complexes are found in the Cambridge Structure Database (CSD version 5.45, update of June 2024; Groom *et al.*, 2016). A search of the CSD for dinuclear copper(II) complexes derived

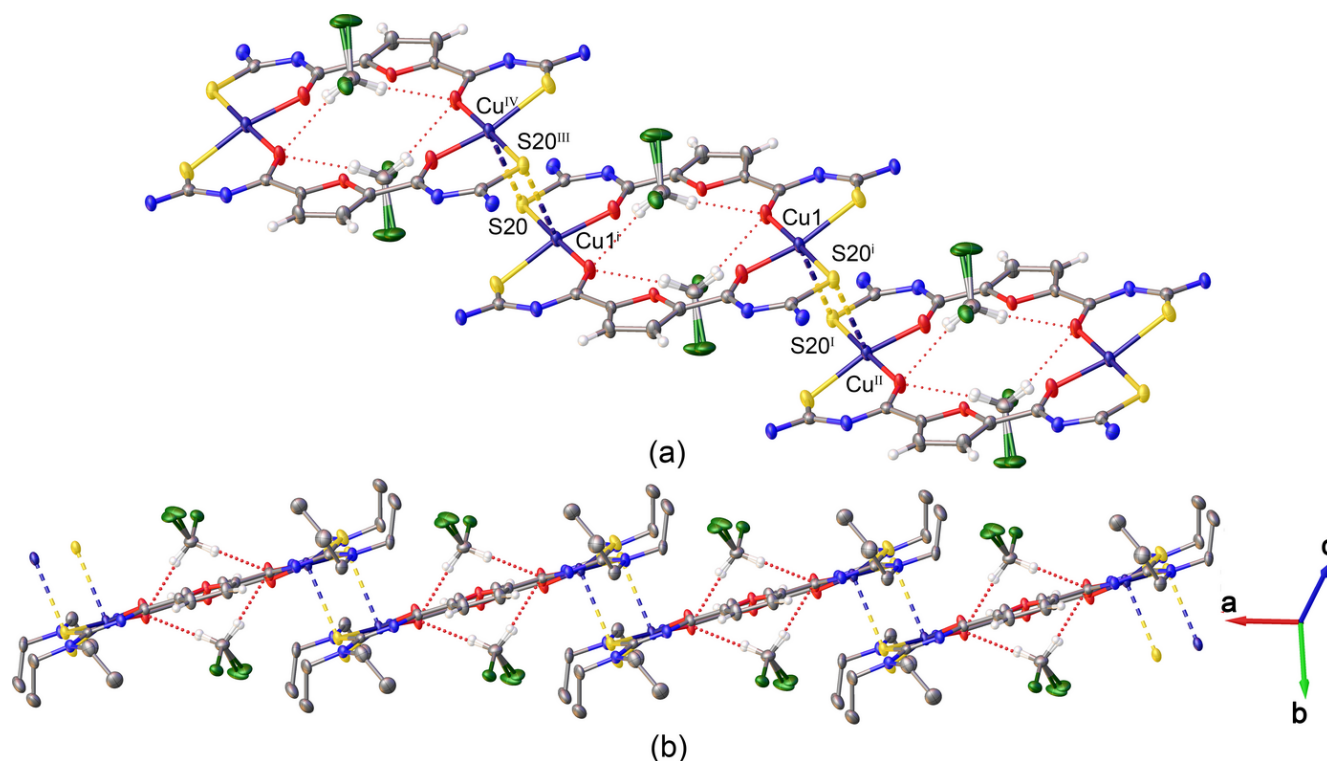


Figure 2

(a) Molecular packing of $[\text{Cu}_2(\text{L})_2] \cdot 2\text{CH}_2\text{Cl}_2$ units by coordinative $\text{Cu} \cdots \text{S}$ interactions (dashed lines). Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (I) $x + 1, y, z$; (II) $-x + 2, -y + 1, -z + 1$; (III) $-x, -y + 1, -z + 1$; (IV) $x - 1, y, z$. Ethyl groups are omitted for clarity. (b) Polymeric chains along the a -axis direction. Hydrogen atoms of ethyl groups are omitted for clarity.

from aroylbis(thioureas) reveals only five hits involving isophthaloyl derivatives: DIZTEM and DIZTEM1 (Rodenstein *et al.*, 2008), BEWKAR (Schwade *et al.*, 2013), DOMNIE (Selvakumaran *et al.*, 2014) and YUFNUL (Teixeira *et al.*, 2020). Across the series of metrics for these structures, all values regarding the coordination of copper(II) ions and

aroylthiourea moieties are in accordance with those reported herein.

5. Synthesis and crystallization

H₂L (38.5 mg, 0.1 mmol) was added into a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.1 mg, 0.1 mmol) in 1 mL of MeOH. The reaction mixture was stirred at 313 K for 30 min before adding the supporting base Et_3N (0.03 mL, 0.2 mmol). A brown precipitate deposited immediately. After stirring for additional 1 h at 313 K, the product was filtered off, washed with MeOH, and dried under reduced pressure. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in a mixture of CH_2Cl_2 and MeOH. Under ambient conditions, the crystals slowly turned to powder due to the evaporation of the co-crystallized solvent.

IR (KBr, cm^{-1}): 2974 (w), 2931 (w), 1536 (s), 1492 (s), 1455 (m), 1399 (s), 1373 (s), 1348 (s), 1304 (s), 1262 (s), 1219 (m), 1148 (m), 1111 (m), 1074 (m), 1008 (s), 9722 (m), 880 (s), 813 (s), 767 (s), 665 (m), 6155 (w), 548 (w), 455 (m).

+ESI MS (m/z): 893.19 (calculated 893.09), 50% $[\text{Cu}_2(\text{L})_2 + \text{H}]^+$; 931.24 (calculated 931.05), 100% $[\text{Cu}_2(\text{L})_2 + \text{K}]^+$.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were placed at calculated positions and refined in riding mode, with C—H

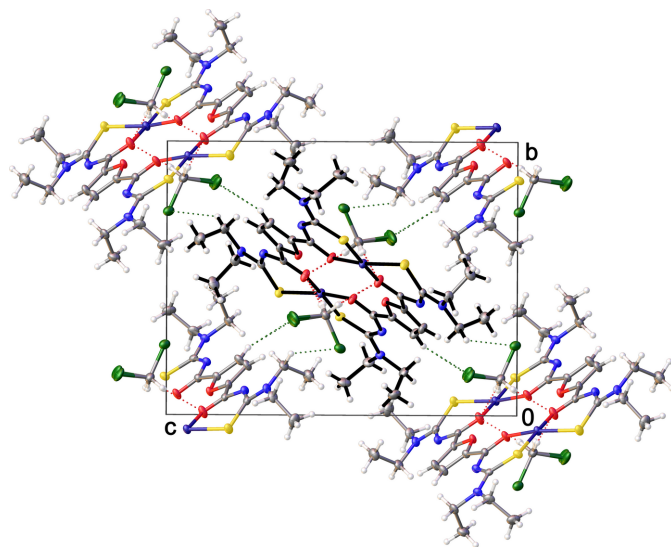


Figure 3

Crystal packing of the title compound shown in projection down the a -axis illustrating the aggregation of chains by $\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonding (green dotted lines). The central units are highlighted for clarity.

distances of 0.95 Å (aromatic), 0.99 Å (CH₂) and 0.98 Å (CH₃), and isotropic displacement parameters equal to 1.2U_{eq} of the parent atoms (1.5U_{eq} for CH₃).

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Table 2
Experimental details.

Crystal data	
Chemical formula	[Cu ₂ (C ₁₆ H ₂₂ N ₄ O ₃ S ₂) ₂].2CH ₂ Cl ₂
<i>M_r</i>	1061.92
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	140
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2290 (9), 13.0681 (10), 16.9601 (15)
β (°)	98.377 (3)
<i>V</i> (Å ³)	2242.9 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.42
Crystal size (mm)	0.14 × 0.08 × 0.05
Data collection	
Diffractionmeter	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.686, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	29179, 5809, 4232
<i>R</i> _{int}	0.062
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.677
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.038, 0.076, 1.03
No. of reflections	5809
No. of parameters	276
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.50, -0.45

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Crystal structure of a solvated dinuclear Cu^{II} complex derived from 3,3,3',3'-tetraethyl-1,1'-(furan-2,5-dicarbonyl)bis(thiourea)

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Computing details

Bis[μ -3,3,3',3'-tetraethyl-1,1'-(furan-2,5-dicarbonyl)bis(thioureato)]dicopper(II) dichloromethane disolvate

Crystal data

[Cu₂(C₁₆H₂₂N₄O₃S₂)₂].2CH₂Cl₂

$M_r = 1061.92$

Monoclinic, $P2_1/n$

$a = 10.2290$ (9) Å

$b = 13.0681$ (10) Å

$c = 16.9601$ (15) Å

$\beta = 98.377$ (3)°

$V = 2242.9$ (3) Å³

$Z = 2$

$F(000) = 1092$

$D_x = 1.572$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8429 reflections

$\theta = 2.9$ – 28.6 °

$\mu = 1.42$ mm⁻¹

$T = 140$ K

Plate, red

$0.14 \times 0.08 \times 0.05$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.686$, $T_{\max} = 0.746$

29179 measured reflections

5809 independent reflections

4232 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 28.8$ °, $\theta_{\min} = 2.9$ °

$h = -13 \rightarrow 12$

$k = -16 \rightarrow 17$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.076$

$S = 1.03$

5809 reflections

276 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.9669P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.50$ e Å⁻³

$\Delta\rho_{\min} = -0.44$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.84517 (2)	0.55425 (2)	0.43977 (2)	0.01612 (8)	
S20	-0.02763 (5)	0.36002 (4)	0.50470 (3)	0.01813 (12)	
S10	0.92190 (5)	0.55137 (4)	0.32124 (3)	0.02175 (13)	
Cl1	0.51955 (6)	0.24405 (4)	0.50494 (4)	0.02871 (14)	
Cl2A	0.6845 (12)	0.3546 (8)	0.6351 (5)	0.0389 (13)	0.62 (6)
O1	0.43749 (13)	0.41530 (10)	0.37590 (8)	0.0148 (3)	
O20	0.24820 (14)	0.42489 (11)	0.46961 (9)	0.0201 (3)	
O10	0.67999 (14)	0.49014 (12)	0.39462 (9)	0.0234 (4)	
N20	0.12097 (16)	0.30601 (13)	0.38549 (10)	0.0161 (4)	
N10	0.72045 (17)	0.41079 (13)	0.27587 (11)	0.0171 (4)	
N21	-0.06963 (17)	0.22096 (13)	0.39037 (11)	0.0174 (4)	
N11	0.90007 (17)	0.40368 (13)	0.21277 (11)	0.0181 (4)	
C20	0.2228 (2)	0.36677 (15)	0.40972 (12)	0.0155 (4)	
C21	0.01399 (19)	0.29379 (15)	0.42245 (12)	0.0149 (4)	
C10	0.6509 (2)	0.43597 (15)	0.33275 (12)	0.0146 (4)	
C5	0.3243 (2)	0.35962 (15)	0.35652 (13)	0.0156 (4)	
C2	0.5189 (2)	0.38896 (16)	0.32183 (12)	0.0150 (4)	
C11	0.8417 (2)	0.44890 (16)	0.26910 (12)	0.0165 (4)	
C4	0.3331 (2)	0.29970 (17)	0.29214 (14)	0.0226 (5)	
H4	0.267641	0.253875	0.267244	0.027*	
C12	1.0320 (2)	0.43485 (17)	0.19544 (14)	0.0221 (5)	
H12A	1.076331	0.374578	0.175901	0.026*	
H12B	1.085855	0.457912	0.245532	0.026*	
C14	0.8325 (2)	0.31971 (17)	0.16420 (13)	0.0229 (5)	
H14A	0.784256	0.276870	0.198538	0.027*	
H14B	0.899900	0.276039	0.144445	0.027*	
C3	0.4587 (2)	0.31868 (17)	0.26922 (13)	0.0218 (5)	
H3	0.493828	0.288489	0.225885	0.026*	
C22	-0.1906 (2)	0.19430 (17)	0.42337 (14)	0.0237 (5)	
H22A	-0.255015	0.163290	0.380844	0.028*	
H22B	-0.230516	0.257583	0.441381	0.028*	
C30	0.5687 (2)	0.36547 (17)	0.54694 (14)	0.0244 (5)	
H30A	0.608215	0.406292	0.507265	0.029*	0.62 (6)
H30B	0.489631	0.402474	0.559208	0.029*	0.62 (6)
H30C	0.620516	0.402930	0.511272	0.029*	0.38 (6)
H30D	0.489701	0.406736	0.553233	0.029*	0.38 (6)
C24	-0.0367 (2)	0.15816 (17)	0.32306 (14)	0.0233 (5)	
H24A	-0.002603	0.203498	0.283944	0.028*	
H24B	-0.118227	0.125169	0.296061	0.028*	
C23	-0.1646 (3)	0.12006 (18)	0.49296 (16)	0.0324 (6)	
H23A	-0.122811	0.057995	0.475893	0.049*	
H23B	-0.248397	0.102117	0.511037	0.049*	
H23C	-0.105823	0.152244	0.536775	0.049*	
C15	0.7365 (3)	0.3571 (2)	0.09391 (15)	0.0333 (6)	
H15A	0.784371	0.396006	0.057839	0.050*	

H15B	0.670058	0.401186	0.112873	0.050*	
H15C	0.692659	0.298337	0.065448	0.050*	
C13	1.0272 (3)	0.5201 (2)	0.13398 (16)	0.0336 (6)	
H13A	0.975577	0.497390	0.083784	0.050*	
H13B	1.117258	0.536891	0.125049	0.050*	
H13C	0.985739	0.580787	0.153507	0.050*	
C25	0.0658 (3)	0.07585 (18)	0.34959 (17)	0.0336 (6)	
H25A	0.087206	0.038988	0.302800	0.050*	
H25B	0.030115	0.027765	0.385352	0.050*	
H25C	0.145957	0.107842	0.377676	0.050*	
Cl2B	0.6656 (19)	0.3460 (10)	0.6407 (9)	0.044 (2)	0.38 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01290 (13)	0.02103 (14)	0.01530 (14)	−0.00403 (10)	0.00497 (10)	−0.00410 (11)
S20	0.0141 (3)	0.0184 (3)	0.0231 (3)	−0.0034 (2)	0.0069 (2)	−0.0044 (2)
S10	0.0214 (3)	0.0267 (3)	0.0191 (3)	−0.0083 (2)	0.0096 (2)	−0.0042 (2)
Cl1	0.0350 (3)	0.0237 (3)	0.0301 (3)	0.0012 (2)	0.0136 (3)	0.0036 (2)
Cl2A	0.041 (2)	0.045 (2)	0.0275 (12)	0.006 (2)	−0.0045 (13)	0.0173 (14)
O1	0.0119 (7)	0.0207 (7)	0.0127 (8)	−0.0033 (6)	0.0046 (6)	−0.0045 (6)
O20	0.0158 (7)	0.0274 (8)	0.0184 (8)	−0.0086 (6)	0.0074 (6)	−0.0106 (6)
O10	0.0135 (8)	0.0379 (9)	0.0199 (9)	−0.0081 (7)	0.0067 (6)	−0.0118 (7)
N20	0.0125 (9)	0.0177 (9)	0.0181 (10)	−0.0029 (7)	0.0023 (7)	−0.0029 (7)
N10	0.0156 (9)	0.0200 (9)	0.0168 (10)	−0.0010 (7)	0.0063 (8)	−0.0021 (7)
N21	0.0133 (9)	0.0172 (9)	0.0217 (10)	−0.0030 (7)	0.0022 (7)	−0.0021 (7)
N11	0.0150 (9)	0.0240 (9)	0.0166 (10)	0.0002 (7)	0.0068 (8)	−0.0021 (8)
C20	0.0142 (10)	0.0174 (10)	0.0146 (11)	−0.0015 (8)	0.0014 (9)	−0.0008 (8)
C21	0.0124 (10)	0.0134 (10)	0.0184 (11)	0.0005 (8)	0.0010 (9)	0.0019 (8)
C10	0.0144 (10)	0.0163 (10)	0.0129 (11)	0.0013 (8)	0.0018 (8)	0.0019 (8)
C5	0.0124 (10)	0.0177 (10)	0.0165 (11)	−0.0032 (8)	0.0010 (8)	−0.0025 (8)
C2	0.0141 (10)	0.0204 (11)	0.0114 (11)	0.0029 (8)	0.0046 (8)	−0.0012 (8)
C11	0.0156 (10)	0.0199 (10)	0.0141 (11)	0.0012 (9)	0.0022 (8)	0.0026 (9)
C4	0.0173 (11)	0.0275 (12)	0.0232 (13)	−0.0066 (9)	0.0036 (10)	−0.0097 (10)
C12	0.0134 (11)	0.0320 (12)	0.0224 (12)	0.0028 (9)	0.0078 (9)	−0.0027 (10)
C14	0.0230 (12)	0.0251 (12)	0.0222 (13)	0.0030 (10)	0.0084 (10)	−0.0045 (9)
C3	0.0201 (11)	0.0279 (12)	0.0189 (12)	−0.0038 (9)	0.0079 (10)	−0.0092 (9)
C22	0.0142 (11)	0.0241 (12)	0.0331 (14)	−0.0086 (9)	0.0044 (10)	−0.0022 (10)
C30	0.0273 (13)	0.0233 (12)	0.0222 (13)	0.0032 (10)	0.0028 (10)	0.0042 (9)
C24	0.0221 (12)	0.0257 (12)	0.0215 (12)	−0.0086 (10)	0.0013 (10)	−0.0080 (9)
C23	0.0313 (14)	0.0234 (13)	0.0458 (17)	−0.0043 (11)	0.0165 (12)	0.0046 (11)
C15	0.0300 (14)	0.0382 (15)	0.0303 (15)	−0.0026 (11)	−0.0004 (11)	−0.0064 (11)
C13	0.0251 (13)	0.0474 (16)	0.0303 (15)	−0.0067 (12)	0.0108 (11)	0.0089 (12)
C25	0.0389 (15)	0.0242 (13)	0.0392 (16)	0.0012 (11)	0.0106 (13)	−0.0070 (11)
Cl2B	0.056 (4)	0.043 (2)	0.027 (3)	−0.021 (3)	−0.016 (3)	0.0175 (18)

Geometric parameters (Å, °)

Cu1—S20 ⁱ	2.2612 (6)	C12—H12B	0.9900
Cu1—S10	2.2624 (6)	C12—C13	1.521 (3)
Cu1—O20 ⁱ	1.9431 (14)	C14—H14A	0.9900
Cu1—O10	1.9406 (15)	C14—H14B	0.9900
S20—C21	1.746 (2)	C14—C15	1.511 (3)
S10—C11	1.743 (2)	C3—H3	0.9500
C11—C30	1.781 (2)	C22—H22A	0.9900
Cl2A—C30	1.773 (8)	C22—H22B	0.9900
O1—C5	1.366 (2)	C22—C23	1.521 (3)
O1—C2	1.369 (2)	C30—H30A	0.9900
O20—C20	1.265 (2)	C30—H30B	0.9900
O10—C10	1.265 (2)	C30—H30C	0.9900
N20—C20	1.326 (3)	C30—H30D	0.9900
N20—C21	1.347 (3)	C30—Cl2B	1.766 (13)
N10—C10	1.321 (3)	C24—H24A	0.9900
N10—C11	1.357 (3)	C24—H24B	0.9900
N21—C21	1.341 (3)	C24—C25	1.523 (3)
N21—C22	1.472 (3)	C23—H23A	0.9800
N21—C24	1.484 (3)	C23—H23B	0.9800
N11—C11	1.336 (3)	C23—H23C	0.9800
N11—C12	1.479 (3)	C15—H15A	0.9800
N11—C14	1.481 (3)	C15—H15B	0.9800
C20—C5	1.475 (3)	C15—H15C	0.9800
C10—C2	1.471 (3)	C13—H13A	0.9800
C5—C4	1.357 (3)	C13—H13B	0.9800
C2—C3	1.363 (3)	C13—H13C	0.9800
C4—H4	0.9500	C25—H25A	0.9800
C4—C3	1.417 (3)	C25—H25B	0.9800
C12—H12A	0.9900	C25—H25C	0.9800
S20 ⁱ —Cu1—S10	90.35 (2)	C2—C3—C4	106.24 (19)
O20 ⁱ —Cu1—S20 ⁱ	94.14 (4)	C2—C3—H3	126.9
O20 ⁱ —Cu1—S10	168.29 (5)	C4—C3—H3	126.9
O10—Cu1—S20 ⁱ	175.25 (5)	N21—C22—H22A	109.1
O10—Cu1—S10	92.12 (5)	N21—C22—H22B	109.1
O10—Cu1—O20 ⁱ	82.68 (6)	N21—C22—C23	112.59 (19)
C21—S20—Cu1 ⁱ	107.20 (7)	H22A—C22—H22B	107.8
C11—S10—Cu1	105.37 (7)	C23—C22—H22A	109.1
C5—O1—C2	106.35 (15)	C23—C22—H22B	109.1
C20—O20—Cu1 ⁱ	130.70 (13)	Cl1—C30—H30A	109.1
C10—O10—Cu1	130.91 (13)	Cl1—C30—H30B	109.1
C20—N20—C21	125.52 (18)	Cl1—C30—H30C	110.0
C10—N10—C11	124.50 (18)	Cl1—C30—H30D	110.0
C21—N21—C22	122.38 (18)	Cl2A—C30—Cl1	112.4 (4)
C21—N21—C24	120.11 (17)	Cl2A—C30—H30A	109.1
C22—N21—C24	117.34 (17)	Cl2A—C30—H30B	109.1

C11—N11—C12	122.41 (18)	H30A—C30—H30B	107.9
C11—N11—C14	120.30 (17)	H30C—C30—H30D	108.3
C12—N11—C14	117.29 (17)	C12B—C30—C11	108.7 (5)
O20—C20—N20	131.98 (19)	C12B—C30—H30C	110.0
O20—C20—C5	116.66 (17)	C12B—C30—H30D	110.0
N20—C20—C5	111.33 (18)	N21—C24—H24A	109.0
N20—C21—S20	128.46 (16)	N21—C24—H24B	109.0
N21—C21—S20	117.42 (15)	N21—C24—C25	112.76 (19)
N21—C21—N20	114.12 (18)	H24A—C24—H24B	107.8
O10—C10—N10	131.22 (19)	C25—C24—H24A	109.0
O10—C10—C2	116.03 (17)	C25—C24—H24B	109.0
N10—C10—C2	112.72 (18)	C22—C23—H23A	109.5
O1—C5—C20	117.82 (17)	C22—C23—H23B	109.5
C4—C5—O1	110.36 (17)	C22—C23—H23C	109.5
C4—C5—C20	131.58 (19)	H23A—C23—H23B	109.5
O1—C2—C10	116.58 (17)	H23A—C23—H23C	109.5
C3—C2—O1	110.28 (18)	H23B—C23—H23C	109.5
C3—C2—C10	133.07 (19)	C14—C15—H15A	109.5
N10—C11—S10	127.42 (16)	C14—C15—H15B	109.5
N11—C11—S10	118.44 (15)	C14—C15—H15C	109.5
N11—C11—N10	114.05 (18)	H15A—C15—H15B	109.5
C5—C4—H4	126.6	H15A—C15—H15C	109.5
C5—C4—C3	106.76 (19)	H15B—C15—H15C	109.5
C3—C4—H4	126.6	C12—C13—H13A	109.5
N11—C12—H12A	108.9	C12—C13—H13B	109.5
N11—C12—H12B	108.9	C12—C13—H13C	109.5
N11—C12—C13	113.50 (19)	H13A—C13—H13B	109.5
H12A—C12—H12B	107.7	H13A—C13—H13C	109.5
C13—C12—H12A	108.9	H13B—C13—H13C	109.5
C13—C12—H12B	108.9	C24—C25—H25A	109.5
N11—C14—H14A	108.9	C24—C25—H25B	109.5
N11—C14—H14B	108.9	C24—C25—H25C	109.5
N11—C14—C15	113.34 (19)	H25A—C25—H25B	109.5
H14A—C14—H14B	107.7	H25A—C25—H25C	109.5
C15—C14—H14A	108.9	H25B—C25—H25C	109.5
C15—C14—H14B	108.9		
Cu1 ⁱ —S20—C21—N20	-14.0 (2)	C10—N10—C11—S10	-11.0 (3)
Cu1 ⁱ —S20—C21—N21	166.21 (14)	C10—N10—C11—N11	172.43 (19)
Cu1—S10—C11—N10	29.0 (2)	C10—C2—C3—C4	176.6 (2)
Cu1—S10—C11—N11	-154.56 (15)	C5—O1—C2—C10	-177.26 (17)
Cu1 ⁱ —O20—C20—N20	5.2 (4)	C5—O1—C2—C3	0.3 (2)
Cu1 ⁱ —O20—C20—C5	-172.26 (14)	C5—C4—C3—C2	0.4 (3)
Cu1—O10—C10—N10	-5.1 (3)	C2—O1—C5—C20	175.01 (18)
Cu1—O10—C10—C2	172.61 (14)	C2—O1—C5—C4	0.0 (2)
O1—C5—C4—C3	-0.2 (3)	C11—N10—C10—O10	-6.7 (4)
O1—C2—C3—C4	-0.4 (3)	C11—N10—C10—C2	175.57 (19)
O20—C20—C5—O1	0.3 (3)	C11—N11—C12—C13	-88.5 (3)

O20—C20—C5—C4	174.1 (2)	C11—N11—C14—C15	83.8 (2)
O10—C10—C2—O1	5.2 (3)	C12—N11—C11—S10	2.4 (3)
O10—C10—C2—C3	-171.6 (2)	C12—N11—C11—N10	179.34 (18)
N20—C20—C5—O1	-177.58 (17)	C12—N11—C14—C15	-95.6 (2)
N20—C20—C5—C4	-3.8 (3)	C14—N11—C11—S10	-176.94 (15)
N10—C10—C2—O1	-176.69 (17)	C14—N11—C11—N10	0.0 (3)
N10—C10—C2—C3	6.5 (3)	C14—N11—C12—C13	90.9 (2)
C20—N20—C21—S20	6.1 (3)	C22—N21—C21—S20	-1.7 (3)
C20—N20—C21—N21	-174.10 (19)	C22—N21—C21—N20	178.48 (18)
C20—C5—C4—C3	-174.3 (2)	C22—N21—C24—C25	-98.7 (2)
C21—N20—C20—O20	0.9 (4)	C24—N21—C21—S20	-176.80 (15)
C21—N20—C20—C5	178.46 (19)	C24—N21—C21—N20	3.4 (3)
C21—N21—C22—C23	-82.9 (2)	C24—N21—C22—C23	92.4 (2)
C21—N21—C24—C25	76.7 (2)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C30—H30A \cdots O10	0.99	2.41	3.388 (3)	171
C30—H30B \cdots O10 ⁱ	0.99	2.45	3.428 (3)	171
C14—H14B \cdots C11 ⁱⁱ	0.99	2.83	3.627 (2)	138
C4—H4 \cdots C12A ⁱⁱⁱ	0.95	2.68	3.506 (8)	145
C4—H4 \cdots C12B ⁱⁱⁱ	0.95	2.60	3.446 (12)	149

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1/2, -y+1/2, z-1/2$; (iii) $x-1/2, -y+1/2, z-1/2$.