

Crystal structure of the [(1,3-dimesityl-1*H*-imidazol-3-ium-2-yl)methanolato]copper(II) chloride dimer: insertion of formaldehyde into a copper–carbene bond

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¹ Insertion of formaldehyde into a copper–carbene bond.

Keywords: crystal structure; copper; N-heterocyclic carbene; insertion; formaldehyde.

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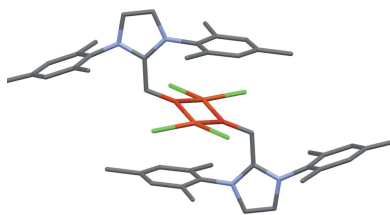
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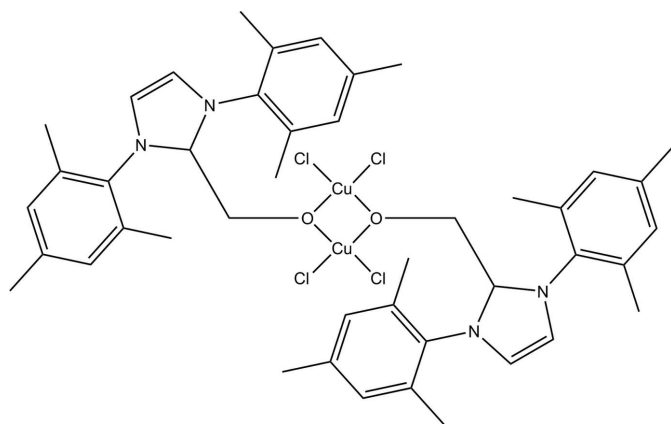
The crystal structure of bis[μ -(1,3-dimesityl-1*H*-imidazol-3-ium-2-yl)methanolato- κ^2 O:O]bis[dichloridocopper(II)], [Cu₂Cl₄(C₂₂H₂₆N₂O)₂], is reported. The complex is assumed to have formed *via* the insertion of formaldehyde into the copper–carbon bond in an N-heterocyclic carbene complex of copper(I) chloride. The structure of the binuclear molecule possesses a crystallographically centrosymmetric Cu₂O₂ central core with the O atoms bridging between the Cu^{II} atoms and thus $Z' = 0.5$. The copper centres are further ligated by two chloride ligands, resulting in the Cu^{II} atoms residing in a distorted square-planar environment. The Cu–O bond lengths are shorter than those previously reported in structures with the same central Cu₂O₂ motif. The complex displays C–H \cdots Cl interactions involving the H atoms of the heterocycle backbone and the chloride ligands of a neighbouring molecule.

1. Chemical context

The chemistry of N-heterocyclic carbene (NHC) ligands is prominent within the landscape of inorganic and organometallic chemistry and now, more than 25 years on from Arduengo's land-mark paper (Arduengo *et al.*, 1991), this prominence looks set to continue. One area that has proven fruitful is the chemistry of NHCs with the group 11 transition metal elements. In particular, the chemistry with copper has resulted in an abundance of complexes that have proven to be effective catalysts for a range of organic transformations, including conjugate addition and carboxylation (Egbert *et al.*, 2013). The preparation of neutral mono-NHC complexes with the general formulae [Cu(NHC)Cl] is routine and straightforward with a variety of synthetic routes to such species available (McLean *et al.*, 2010; Santoro *et al.*, 2013; Gibard *et al.*, 2013; Lake *et al.*, 2012). One of the simplest routes is the reaction of imidazol(in)ium chloride with Cu₂O under reflux conditions with no requirement for the exclusion of air and water. The species formed are stable when they are isolated in the solid state but solutions show signs of oxidation upon standing for prolonged periods, especially when they are prepared in coordinating solvents such as THF or acetonitrile. The tell-tale green colour, which indicates the formation of copper(II) species, is surely a common observation for chemists who work with copper(I)–NHC species, but surprisingly the literature offers little on the identification of these species and corresponding reaction pathways. This is most likely a consequence of the inherent difficulty in character-



izing the paramagnetic copper(II) species formed. Our interest in this area has previously revolved around the modification of [Cu(NHC)Cl] complexes through the replacement of the chloride ligand with the thiocyanate ligand (Dodds & Kennedy, 2014). Herein we report the formation of the unusual (1,3-dimesityl-1*H*-imidazol-3-ium-2-yl) copper(II) chloride dimer, formed presumably from the insertion of formaldehyde into the Cu–NHC bond, upon prolonged standing of a THF solution containing [Cu(IMes)Cl] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] and trace amounts of formaldehyde at 255 K. The presence of formaldehyde was a result of the preparation of the imidazolium chloride precursor, which utilises paraformaldehyde. Evidently trace amounts of paraformaldehyde have been present during the reflux of Cu₂O with imidazolium chloride, with the resulting solution generating the reported complex upon prolonged standing. This is the first structurally characterized example of a species formed through the insertion of a small molecule into a copper–NHC bond. To date, all attempts to prepare the complex rationally have proven unsuccessful.



2. Structural commentary

The structure of the binuclear molecule (I) consists of a Cu₂O₂Cl₄ central core, possessing a Cu₂O₂ four-membered ring with each copper centre further coordinated by two chloride ligands. Each dimer is sited around a crystallographic centre of symmetry and thus $Z' = 0.5$. The structure of the asymmetric unit, with atom labels, is given in Fig. 1 and the dimeric unit is shown in Fig. 2. The copper centres reside in a distorted square-planar environment, as can be evidenced by the O–Cu–O and Cl–Cu–Cl bond angles [74.10 (11) and 97.58 (5)° respectively], which both deviate markedly from 90°. This distortion from ideal square planar geometry is further illustrated by the *trans* O–Cu–Cl bond angles [162.46 (10) and 162.36 (9)°], which also deviate noticeably from the expected 180°. Similar Cu₂O₂Cl₄ central cores have been observed previously by a number of groups (Schäfer *et al.*, 1965; Sager *et al.*, 1967; Watson & Johnson, 1971; Ivashevskaja *et al.*, 2002) with a similar distortion around the Cu^{II} atom observed. The Cu–O and Cu–Cl bond lengths are 1.934 (3) and 1.944 (3) Å and 2.2326 (13) and 2.2395 (12) Å,

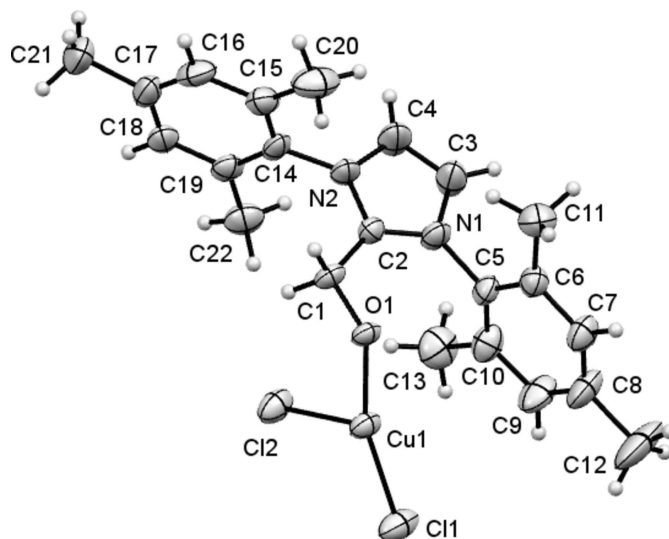


Figure 1

View of the contents of the asymmetric unit of (I). Non-H atoms are drawn as 50% probability ellipsoids and H atoms as small spheres of arbitrary size.

respectively. The Cu–O bond lengths are shorter than those observed in these previous reports [1.979–2.106 Å] while the Cu–Cl bond distances compare well to the previously reported examples [2.205–2.243 Å]. Finally, with regards to the central core, the Cu···Cu and O···O internuclear distances are 3.0950 (12) and 2.337 (5) Å, respectively. The O···O distance is comparable to previous reports [2.366–2.591 Å] while the Cu···Cu distance is appreciably shorter when the comparison is made [3.190–3.245 Å]. The C–O bond length is 1.398 (4) Å, which is comparable with a structure previously reported by Hevia and co-workers (Uzelac *et al.*, 2016) in which the zwitterion [ItBuCH₂OgAr₃] [where ItBu = 1,3-bis(*tert*-butyl)imidazol-2-ylidene; R = trimethylsilylmethyl] displays a C–O bond length of 1.384 (3) Å. The new C–C bond formed has a bond length of 1.497 (6) Å, which again compares well with the equivalent bond in the aforementioned zwitterion [1.505 (3) Å]. The imidazolium ring is positioned such that it forms a dihedral angle of 90° with the plane of the Cu₂O₂ ring, torsion angle O1–C1–C2–N1 = 0.2 (7)°. This *syn* arrangement results in the C5–C10 mesityl rings lying

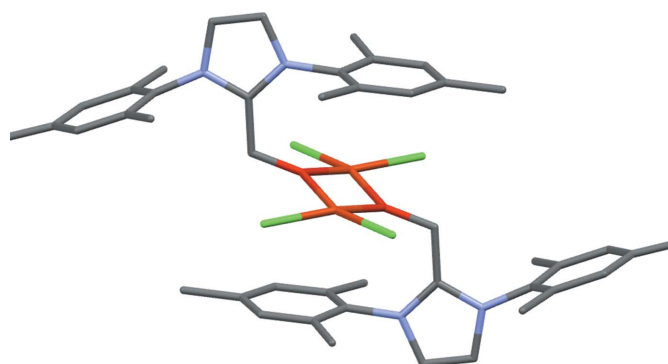


Figure 2

Molecular structure of dimeric (I). The two halves of the dimer are related by $-x, -y + 1, -z + 2$. H atoms are omitted for clarity.

Table 1
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1–H1A \cdots Cl1 ⁱ	0.99	2.59	3.216 (5)	121
C1–H1B \cdots Cl2	0.99	2.54	3.215 (5)	126
C3–H3 \cdots Cl2 ⁱⁱ	0.95	2.51	3.458 (6)	173
C4–H4 \cdots Cl1 ⁱⁱ	0.95	2.76	3.385 (5)	124
C13–H13A \cdots Cl2	0.98	2.79	3.684 (6)	152

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

above and below the Cu₂O₂ ring, as shown in Fig. 2. The distance between the centroids of the Cu₂O₂ ring and the mesityl ring is 3.390 (2) Å.

3. Supramolecular features

The complex exhibits intermolecular C–H \cdots Cl interactions, specifically two short interactions between the H atoms on the unsaturated backbone of the heterocycle and the chloride ligands of a neighbouring molecule at position $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$. The intermolecular H \cdots Cl distances measure 2.51 and 2.76 Å. These interactions combine to give a two-dimensional supramolecular motif that propagates parallel to the (101) plane. Fig. 3 illustrates the C–H \cdots Cl intermolecular interactions and numerical details are given in Table 1.

4. Database survey

Outside the complex reported herein, there are eight structures reported in the Cambridge Structural Database (CSD, Version 5.39, update No. 2, February 2018; Groom *et al.*, 2016) that contain a Cu₂O₂Cl₄ core and in which there is no additional coordination to the Cu^{II} atoms. The majority of structures reported contain pyridine *N*-oxide ligands (Schäfer *et al.*, 1965; refcodes CUCPYO, CUCPYO11 and CUCPYO13; Sager *et al.*, 1967; refcodes QQQBWD, QQQBWG and QQQBWJ; Watson & Johnson, 1971; refcode PHPYOC). The lone example that does not include a pyridine *N*-oxide ligand

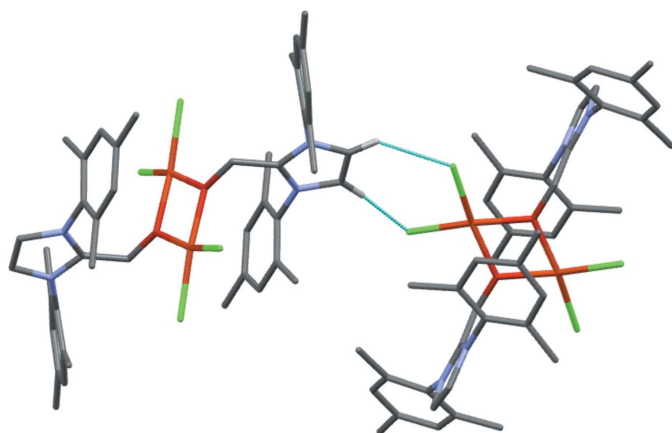


Figure 3
 View highlighting the close Cl \cdots H contacts between neighbouring molecules of (I). See text for details.

Table 2
 Experimental details.

Crystal data	
Chemical formula	[Cu ₂ Cl ₄ (C ₂₂ H ₂₆ N ₂ O) ₂]
M_r	937.77
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	123
a, b, c (Å)	11.1962 (8), 13.5321 (10), 15.5615 (8)
β (°)	107.705 (6)
V (Å ³)	2246.0 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.23
Crystal size (mm)	0.10 × 0.08 × 0.05
Data collection	
Diffractometer	Oxford Diffraction Xcalibur E
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2014)
T_{\min}, T_{\max}	0.993, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10241, 4960, 2814
R_{int}	0.049
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.062, 0.144, 1.05
No. of reflections	4960
No. of parameters	259
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.43, -0.32

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1994), *SHELXL2014* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2008).

instead contains the related quinoline *N*-oxide ligand (Ivashevskaja *et al.*, 2002; refcode HULZOD). We are aware of no previous examples of ligands formed from NHC by an insertion reaction similar to the one reported herein.

5. Synthesis and crystallization

[Cu(IMes)Cl] was prepared according to literature procedures outlined by Abernethy and co-workers (McLean *et al.*, 2010). After isolation of an initial crop of [Cu(IMes)Cl], the filtrate was placed in the freezer (255 K) and left standing for ~6 months. After this time the pale-orange THF solution had changed to a deep green and a small amount of green crystalline solid had precipitated alongside some green powder. This solid was isolated by filtration, yielding 34 mg of solid. The crystalline material isolated was suitable for single crystal X-ray diffraction. Additionally the isolated product was characterized by elemental analysis and ATR FT-IR.

Analysis calculated for C₄₄H₅₂N₄O₂Cl₄Cu₂: C, 56.38; H, 5.55; N, 5.98%. Found: C, 57.26; H, 5.64; N, 5.13%. ATR FT-IR: $\nu = 1502$ (CO) cm⁻¹.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in calculated positions and refined in riding modes. C–H distances were 0.95, 0.99 and 0.98 Å for CH, CH₂ and CH₃

groups, respectively. For CH₃ groups $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and for all other types, $U_{\text{iso}}(\text{H})_i = 1.2U_{\text{eq}}(\text{C})$.

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Crystal structure of the [(1,3-dimesityl-1*H*-imidazol-3-ium-2-yl)methanolato]copper(II) chloride dimer: insertion of formaldehyde into a copper–carbene bond

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

Bis[μ -(1,3-dimesityl-1*H*-imidazol-3-ium-2-yl)methanolato- κ^2 O:O]bis[dichloridocopper(II)]

Crystal data

[Cu₂Cl₄(C₂₂H₂₆N₂O)₂]

$M_r = 937.77$

Monoclinic, $P2_1/n$

$a = 11.1962$ (8) Å

$b = 13.5321$ (10) Å

$c = 15.5615$ (8) Å

$\beta = 107.705$ (6)°

$V = 2246.0$ (3) Å³

$Z = 2$

$F(000) = 972$

$D_x = 1.387$ Mg m⁻³

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

Cell parameters from 2164 reflections

$\theta = 3.0$ – 28.7 °

$\mu = 1.23$ mm⁻¹

$T = 123$ K

Prism, green

0.10 × 0.08 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur E
diffractometer

Radiation source: sealed tube

ω scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.993$, $T_{\max} = 1.000$

10241 measured reflections

4960 independent reflections

2814 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 28.7$ °, $\theta_{\min} = 3.0$ °

$h = -14$ → 14

$k = -18$ → 16

$l = -19$ → 19

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.144$

$S = 1.05$

4960 reflections

259 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.3159P]$

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

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

$\Delta\rho_{\max} = 0.43$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	−0.06291 (5)	0.59936 (4)	0.96249 (3)	0.03601 (19)
Cl1	−0.20608 (13)	0.68984 (10)	1.00019 (8)	0.0548 (4)
Cl2	−0.03916 (12)	0.69819 (10)	0.85340 (7)	0.0489 (4)
O1	0.0280 (3)	0.4888 (2)	0.93419 (16)	0.0318 (7)
N1	−0.1319 (3)	0.3733 (3)	0.7821 (2)	0.0399 (10)
N2	−0.0002 (4)	0.3953 (3)	0.7078 (2)	0.0398 (10)
C1	0.0662 (4)	0.4767 (4)	0.8572 (2)	0.0333 (11)
H1A	0.1493	0.4442	0.8747	0.040*
H1B	0.0754	0.5426	0.8324	0.040*
C2	−0.0235 (4)	0.4165 (3)	0.7853 (3)	0.0321 (11)
C3	−0.1780 (5)	0.3228 (4)	0.7013 (3)	0.0551 (15)
H3	−0.2531	0.2852	0.6824	0.066*
C4	−0.0958 (5)	0.3371 (4)	0.6549 (3)	0.0585 (16)
H4	−0.1024	0.3119	0.5967	0.070*
C5	−0.1998 (4)	0.3750 (4)	0.8489 (3)	0.0350 (11)
C6	−0.1849 (4)	0.2964 (4)	0.9081 (3)	0.0396 (12)
C7	−0.2554 (5)	0.2987 (4)	0.9679 (3)	0.0476 (13)
H7	−0.2456	0.2469	1.0108	0.057*
C8	−0.3382 (5)	0.3731 (5)	0.9669 (3)	0.0604 (16)
C9	−0.3530 (5)	0.4476 (4)	0.9046 (3)	0.0582 (15)
H9	−0.4104	0.4996	0.9038	0.070*
C10	−0.2855 (5)	0.4490 (4)	0.8423 (3)	0.0470 (13)
C11	−0.1024 (5)	0.2100 (4)	0.9088 (3)	0.0574 (15)
H11A	−0.0598	0.1905	0.9712	0.086*
H11B	−0.0399	0.2280	0.8790	0.086*
H11C	−0.1532	0.1548	0.8765	0.086*
C12	−0.4118 (6)	0.3732 (6)	1.0350 (4)	0.104 (3)
H12A	−0.3942	0.3123	1.0706	0.156*
H12B	−0.5018	0.3771	1.0028	0.156*
H12C	−0.3868	0.4303	1.0751	0.156*
C13	−0.3075 (5)	0.5289 (4)	0.7712 (3)	0.0633 (16)
H13A	−0.2279	0.5618	0.7755	0.095*
H13B	−0.3672	0.5773	0.7808	0.095*
H13C	−0.3415	0.4992	0.7113	0.095*
C14	0.1027 (4)	0.4299 (4)	0.6795 (3)	0.0385 (12)
C15	0.2083 (5)	0.3714 (4)	0.6951 (3)	0.0460 (13)
C16	0.3012 (5)	0.4043 (4)	0.6583 (3)	0.0532 (14)
H16	0.3751	0.3659	0.6670	0.064*
C17	0.2875 (5)	0.4917 (4)	0.6093 (3)	0.0492 (14)

C18	0.1831 (5)	0.5488 (4)	0.5989 (3)	0.0433 (13)
H18	0.1762	0.6097	0.5674	0.052*
C19	0.0875 (4)	0.5205 (4)	0.6326 (3)	0.0376 (12)
C20	0.2251 (6)	0.2775 (4)	0.7500 (4)	0.0688 (18)
H20A	0.2424	0.2941	0.8140	0.103*
H20B	0.2955	0.2396	0.7419	0.103*
H20C	0.1484	0.2378	0.7299	0.103*
C21	0.3850 (5)	0.5198 (5)	0.5650 (4)	0.076 (2)
H21A	0.3568	0.4996	0.5015	0.115*
H21B	0.4643	0.4867	0.5959	0.115*
H21C	0.3975	0.5916	0.5687	0.115*
C22	-0.0275 (5)	0.5833 (4)	0.6182 (3)	0.0524 (15)
H22A	-0.0312	0.6085	0.6764	0.079*
H22B	-0.1023	0.5435	0.5900	0.079*
H22C	-0.0240	0.6390	0.5787	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0437 (4)	0.0389 (4)	0.0313 (3)	0.0073 (3)	0.0201 (2)	0.0036 (3)
Cl1	0.0691 (9)	0.0562 (9)	0.0510 (7)	0.0252 (8)	0.0361 (7)	0.0140 (7)
Cl2	0.0570 (8)	0.0511 (8)	0.0478 (7)	0.0139 (7)	0.0297 (6)	0.0161 (6)
O1	0.0394 (18)	0.0363 (18)	0.0253 (14)	0.0041 (15)	0.0180 (13)	-0.0012 (14)
N1	0.042 (2)	0.053 (3)	0.0291 (19)	-0.008 (2)	0.0179 (17)	-0.0087 (19)
N2	0.048 (2)	0.047 (3)	0.0303 (19)	-0.012 (2)	0.0217 (17)	-0.0134 (19)
C1	0.037 (3)	0.041 (3)	0.026 (2)	0.004 (2)	0.0169 (19)	-0.001 (2)
C2	0.040 (3)	0.032 (3)	0.029 (2)	-0.002 (2)	0.0169 (19)	-0.001 (2)
C3	0.060 (4)	0.070 (4)	0.039 (3)	-0.030 (3)	0.021 (2)	-0.018 (3)
C4	0.073 (4)	0.074 (4)	0.037 (3)	-0.029 (3)	0.029 (3)	-0.023 (3)
C5	0.027 (2)	0.044 (3)	0.036 (2)	-0.004 (2)	0.0137 (19)	-0.001 (2)
C6	0.036 (3)	0.045 (3)	0.040 (3)	-0.007 (2)	0.015 (2)	-0.005 (2)
C7	0.050 (3)	0.054 (4)	0.046 (3)	0.001 (3)	0.025 (2)	0.012 (3)
C8	0.054 (4)	0.081 (5)	0.062 (3)	0.009 (3)	0.041 (3)	0.013 (3)
C9	0.050 (3)	0.064 (4)	0.072 (4)	0.023 (3)	0.035 (3)	0.016 (3)
C10	0.043 (3)	0.059 (4)	0.040 (3)	0.001 (3)	0.014 (2)	0.011 (3)
C11	0.061 (4)	0.054 (4)	0.064 (3)	0.001 (3)	0.028 (3)	-0.009 (3)
C12	0.100 (5)	0.136 (7)	0.114 (5)	0.040 (5)	0.089 (5)	0.037 (5)
C13	0.070 (4)	0.062 (4)	0.057 (3)	0.010 (3)	0.018 (3)	0.017 (3)
C14	0.041 (3)	0.053 (3)	0.028 (2)	-0.012 (3)	0.021 (2)	-0.012 (2)
C15	0.061 (4)	0.041 (3)	0.042 (3)	0.000 (3)	0.026 (2)	-0.006 (2)
C16	0.051 (3)	0.063 (4)	0.054 (3)	0.011 (3)	0.027 (3)	-0.014 (3)
C17	0.052 (3)	0.061 (4)	0.043 (3)	-0.021 (3)	0.027 (2)	-0.015 (3)
C18	0.058 (3)	0.046 (3)	0.032 (2)	-0.011 (3)	0.023 (2)	-0.010 (2)
C19	0.045 (3)	0.047 (3)	0.024 (2)	-0.002 (3)	0.014 (2)	-0.008 (2)
C20	0.096 (5)	0.054 (4)	0.064 (3)	0.028 (4)	0.036 (3)	0.004 (3)
C21	0.072 (4)	0.082 (5)	0.097 (4)	-0.031 (4)	0.058 (4)	-0.029 (4)
C22	0.061 (4)	0.062 (4)	0.034 (3)	0.003 (3)	0.016 (2)	-0.006 (3)

Geometric parameters (Å, °)

Cu1—O1	1.934 (3)	C11—H11A	0.9800
Cu1—O1 ⁱ	1.944 (3)	C11—H11B	0.9800
Cu1—C11	2.2326 (13)	C11—H11C	0.9800
Cu1—C12	2.2395 (12)	C12—H12A	0.9800
O1—C1	1.398 (4)	C12—H12B	0.9800
O1—Cu1 ⁱ	1.944 (3)	C12—H12C	0.9800
N1—C2	1.334 (5)	C13—H13A	0.9800
N1—C3	1.386 (6)	C13—H13B	0.9800
N1—C5	1.463 (5)	C13—H13C	0.9800
N2—C2	1.341 (5)	C14—C15	1.381 (7)
N2—C4	1.381 (6)	C14—C19	1.410 (7)
N2—C14	1.432 (5)	C15—C16	1.404 (7)
C1—C2	1.497 (6)	C15—C20	1.511 (7)
C1—H1A	0.9900	C16—C17	1.390 (7)
C1—H1B	0.9900	C16—H16	0.9500
C3—C4	1.345 (6)	C17—C18	1.369 (7)
C3—H3	0.9500	C17—C21	1.507 (6)
C4—H4	0.9500	C18—C19	1.383 (6)
C5—C10	1.368 (6)	C18—H18	0.9500
C5—C6	1.383 (6)	C19—C22	1.502 (6)
C6—C7	1.392 (6)	C20—H20A	0.9800
C6—C11	1.488 (7)	C20—H20B	0.9800
C7—C8	1.365 (7)	C20—H20C	0.9800
C7—H7	0.9500	C21—H21A	0.9800
C8—C9	1.374 (7)	C21—H21B	0.9800
C8—C12	1.528 (6)	C21—H21C	0.9800
C9—C10	1.398 (6)	C22—H22A	0.9800
C9—H9	0.9500	C22—H22B	0.9800
C10—C13	1.513 (7)	C22—H22C	0.9800
O1—Cu1—O1 ⁱ	74.10 (11)	C6—C11—H11C	109.5
O1—Cu1—C11	162.46 (10)	H11A—C11—H11C	109.5
O1 ⁱ —Cu1—C11	95.69 (9)	H11B—C11—H11C	109.5
O1—Cu1—C12	95.60 (8)	C8—C12—H12A	109.5
O1 ⁱ —Cu1—C12	162.36 (9)	C8—C12—H12B	109.5
C11—Cu1—C12	97.58 (5)	H12A—C12—H12B	109.5
C1—O1—Cu1	127.2 (3)	C8—C12—H12C	109.5
C1—O1—Cu1 ⁱ	126.8 (3)	H12A—C12—H12C	109.5
Cu1—O1—Cu1 ⁱ	105.90 (11)	H12B—C12—H12C	109.5
C2—N1—C3	109.5 (4)	C10—C13—H13A	109.5
C2—N1—C5	129.0 (4)	C10—C13—H13B	109.5
C3—N1—C5	121.5 (4)	H13A—C13—H13B	109.5
C2—N2—C4	109.3 (4)	C10—C13—H13C	109.5
C2—N2—C14	127.0 (4)	H13A—C13—H13C	109.5
C4—N2—C14	123.6 (3)	H13B—C13—H13C	109.5
O1—C1—C2	113.2 (3)	C15—C14—C19	123.5 (4)

O1—C1—H1A	108.9	C15—C14—N2	119.0 (5)
C2—C1—H1A	108.9	C19—C14—N2	117.5 (4)
O1—C1—H1B	108.9	C14—C15—C16	116.6 (5)
C2—C1—H1B	108.9	C14—C15—C20	122.3 (5)
H1A—C1—H1B	107.8	C16—C15—C20	121.1 (5)
N1—C2—N2	107.2 (4)	C17—C16—C15	121.4 (5)
N1—C2—C1	131.5 (3)	C17—C16—H16	119.3
N2—C2—C1	121.3 (4)	C15—C16—H16	119.3
C4—C3—N1	106.8 (4)	C18—C17—C16	119.6 (5)
C4—C3—H3	126.6	C18—C17—C21	120.9 (5)
N1—C3—H3	126.6	C16—C17—C21	119.4 (5)
C3—C4—N2	107.2 (4)	C17—C18—C19	122.0 (5)
C3—C4—H4	126.4	C17—C18—H18	119.0
N2—C4—H4	126.4	C19—C18—H18	119.0
C10—C5—C6	123.5 (4)	C18—C19—C14	116.9 (5)
C10—C5—N1	117.6 (4)	C18—C19—C22	120.9 (5)
C6—C5—N1	118.5 (4)	C14—C19—C22	122.2 (4)
C5—C6—C7	116.8 (5)	C15—C20—H20A	109.5
C5—C6—C11	123.9 (4)	C15—C20—H20B	109.5
C7—C6—C11	119.3 (5)	H20A—C20—H20B	109.5
C8—C7—C6	121.9 (5)	C15—C20—H20C	109.5
C8—C7—H7	119.0	H20A—C20—H20C	109.5
C6—C7—H7	119.0	H20B—C20—H20C	109.5
C7—C8—C9	119.1 (4)	C17—C21—H21A	109.5
C7—C8—C12	120.0 (5)	C17—C21—H21B	109.5
C9—C8—C12	120.9 (6)	H21A—C21—H21B	109.5
C8—C9—C10	121.6 (5)	C17—C21—H21C	109.5
C8—C9—H9	119.2	H21A—C21—H21C	109.5
C10—C9—H9	119.2	H21B—C21—H21C	109.5
C5—C10—C9	117.0 (5)	C19—C22—H22A	109.5
C5—C10—C13	122.1 (4)	C19—C22—H22B	109.5
C9—C10—C13	120.9 (5)	H22A—C22—H22B	109.5
C6—C11—H11A	109.5	C19—C22—H22C	109.5
C6—C11—H11B	109.5	H22A—C22—H22C	109.5
H11A—C11—H11B	109.5	H22B—C22—H22C	109.5
Cu1—O1—C1—C2	-95.8 (4)	C7—C8—C9—C10	0.1 (9)
Cu1 ⁱ —O1—C1—C2	87.6 (4)	C12—C8—C9—C10	179.5 (6)
C3—N1—C2—N2	0.6 (5)	C6—C5—C10—C9	5.5 (7)
C5—N1—C2—N2	-178.9 (4)	N1—C5—C10—C9	177.7 (5)
C3—N1—C2—C1	-178.0 (5)	C6—C5—C10—C13	-174.4 (5)
C5—N1—C2—C1	2.5 (8)	N1—C5—C10—C13	-2.1 (7)
C4—N2—C2—N1	-0.3 (6)	C8—C9—C10—C5	-2.9 (8)
C14—N2—C2—N1	176.7 (5)	C8—C9—C10—C13	177.0 (5)
C4—N2—C2—C1	178.5 (4)	C2—N2—C14—C15	95.2 (6)
C14—N2—C2—C1	-4.5 (7)	C4—N2—C14—C15	-88.2 (6)
O1—C1—C2—N1	0.2 (7)	C2—N2—C14—C19	-88.1 (5)
O1—C1—C2—N2	-178.3 (4)	C4—N2—C14—C19	88.6 (6)

C2—N1—C3—C4	-0.7 (6)	C19—C14—C15—C16	-2.6 (7)
C5—N1—C3—C4	178.9 (5)	N2—C14—C15—C16	173.9 (4)
N1—C3—C4—N2	0.5 (7)	C19—C14—C15—C20	176.5 (4)
C2—N2—C4—C3	-0.1 (7)	N2—C14—C15—C20	-7.0 (7)
C14—N2—C4—C3	-177.3 (5)	C14—C15—C16—C17	0.5 (7)
C2—N1—C5—C10	90.0 (6)	C20—C15—C16—C17	-178.6 (5)
C3—N1—C5—C10	-89.4 (6)	C15—C16—C17—C18	2.0 (7)
C2—N1—C5—C6	-97.3 (6)	C15—C16—C17—C21	-175.3 (4)
C3—N1—C5—C6	83.2 (6)	C16—C17—C18—C19	-2.6 (7)
C10—C5—C6—C7	-5.0 (7)	C21—C17—C18—C19	174.7 (4)
N1—C5—C6—C7	-177.2 (4)	C17—C18—C19—C14	0.6 (6)
C10—C5—C6—C11	172.9 (5)	C17—C18—C19—C22	-178.4 (4)
N1—C5—C6—C11	0.7 (7)	C15—C14—C19—C18	2.1 (6)
C5—C6—C7—C8	1.9 (8)	N2—C14—C19—C18	-174.5 (4)
C11—C6—C7—C8	-176.1 (5)	C15—C14—C19—C22	-178.9 (4)
C6—C7—C8—C9	0.4 (9)	N2—C14—C19—C22	4.5 (6)
C6—C7—C8—C12	-179.0 (6)		

Symmetry code: (i) $-x, -y+1, -z+2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots C11 ⁱ	0.99	2.59	3.216 (5)	121
C1—H1B \cdots C12	0.99	2.54	3.215 (5)	126
C3—H3 \cdots C12 ⁱⁱ	0.95	2.51	3.458 (6)	173
C4—H4 \cdots C11 ⁱⁱⁱ	0.95	2.76	3.385 (5)	124
C13—H13A \cdots C12	0.98	2.79	3.684 (6)	152

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $-x-1/2, y-1/2, -z+3/2$.