

Crystal structure and Hirshfeld surface analysis of di- μ -chlorido-bis[(acetonitrile- κ N)chlorido(ethyl 5-methyl-1*H*-pyrazole-3-carboxylate- κ^2 N²,O)-copper(II)]

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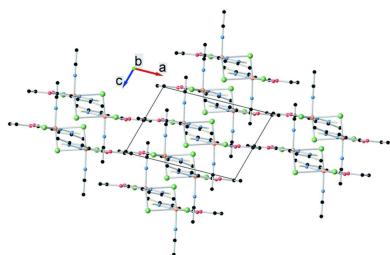
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The title compound, [Cu₂Cl₄(C₅H₁₀N₂O₂)₂(CH₃CN)₂] or [Cu₂(μ -Cl)₂(CH₃—Pz—COOCH₂CH₃)₂Cl₂(CH₃CN)₂], was synthesized using a one-pot reaction of copper powder, copper(II) chloride dihydrate and ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (CH₃—Pz—COOCH₂CH₃) in acetonitrile under ambient conditions. This complex consists of discrete binuclear molecules with a {Cu₂(μ -Cl)₂} core, in which the Cu···Cu distance is 3.8002 (7) Å. The pyrazole-based ligands are bidentate coordinated, leading to the formation of two five-membered chelate rings. The coordination geometry of both copper atoms (ON₂Cl₃) can be described as distorted octahedral on account of the acetonitrile coordination. A Hirshfeld surface analysis suggests that the most important contributions to the surface contacts are from H···H (40%), H···Cl/Cl···H (24.3%), H···O/O···H (11.8%), H···C/C···H (9.2%) and H···N/N···H (8.3%) interactions.

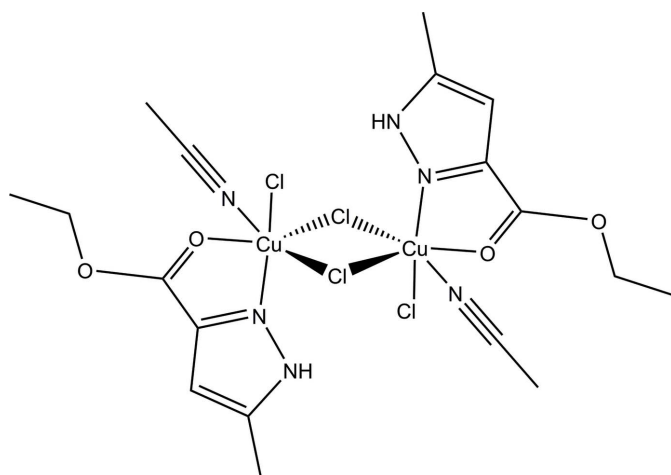
1. Chemical context

Pyrazoles can form structures of various nuclearities, ranging from mononuclear (Mighell *et al.*, 1975; Liu *et al.*, 2001; Mafacka *et al.*, 2003) to polynuclear complexes (He, 2011; Contaldi *et al.*, 2009; Chandrasekhar *et al.*, 2008) and metal-lacycles (Vynohradov *et al.*, 2020*a*; Surmann *et al.*, 2016; Galassi *et al.*, 2012) with specific molecular topologies. By performing the synthesis of metal complexes by oxidative dissolution of metals, commonly known as direct synthesis (Kokozay *et al.*, 2018; Plyuta *et al.*, 2020; Sirenko *et al.*, 2020; Li *et al.*, 2021), copper can be introduced in a zerovalent state. Copper powder can be oxidized in solution in the presence of proton-donating agents, such as pyrazoles, to form polynuclear complexes, where two copper atoms are connected by a bidentate-bridging deprotonated pyrazole (Vynohradov *et al.*, 2020*b*; Davydenko *et al.*, 2013). Many examples of copper coordination compounds have been synthesized and described in which two copper atoms are connected by halogen bridges, for example, through chlorine anions, deprotonated ligand molecules and also hydroxyl groups (Vincent *et al.*, 2018; Wei *et al.*, 2012; Mezei *et al.*, 2004). Copper(II) pyrazolate complexes have attracted considerable interest for their interesting magnetic properties (Malinkin *et al.*, 2012; Spodine *et al.*, 1999) and abilities to bind DNA (Vafazadeh *et al.*, 2015; Kulkarni *et al.*, 2011). Finally, the antioxidant (Kupcewicz *et al.*, 2013) and anticancer (Santini *et al.*, 2014) activities of these



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compounds should be noted. Relatively few unsymmetrical pyrazole-containing ligands with different chelating arms in the 3- and 5-positions and their coordination compounds have been investigated so far (Konrad *et al.*, 2001; Dubs *et al.*, 2006; Krämer *et al.*, 2002; Röder *et al.*, 2002; Penkova *et al.*, 2010). Considering the above, we understand the importance of accumulating a theoretical information base on such coordination compounds, and therefore in this article we report the synthesis, crystal structure and Hirshfeld surface analysis of a new binuclear copper(II) complex with unsymmetrical pyrazole ethyl 5-methyl-1*H*-pyrazole-3-carboxylate – $[\text{Cu}_2(\mu_2\text{-Cl})_2(\text{CH}_3\text{-Pz-COOCH}_2\text{CH}_3)_2\text{Cl}_2(\text{CH}_3\text{CN})_2]$.



2. Structural commentary

The title compound (Fig. 1) is a binuclear cyclic copper(II) pyrazole-containing complex which crystallized in the monoclinic $P2_1/c$ space group. The asymmetric unit consists of one copper ion, one ethyl 5-methyl-1*H*-pyrazole-3-carboxylate

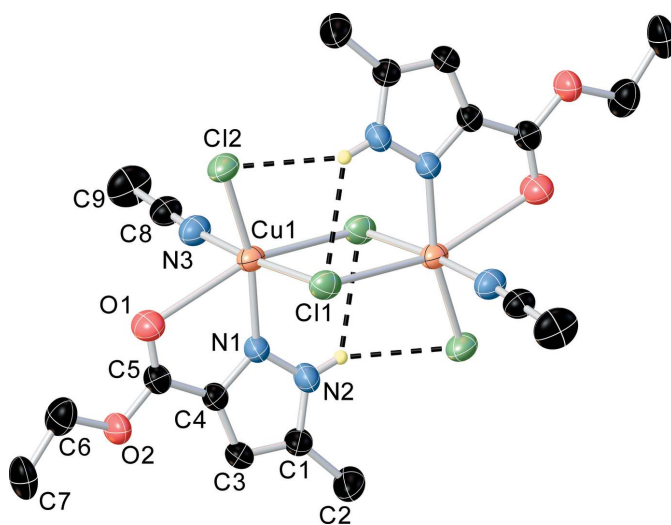


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Irrelevant hydrogen atoms were omitted for clarity.

ligand, one coordinated acetonitrile molecule and two chlorine ions. One of these chlorine ions bridges two metal centers, thus connecting two symmetry-generated fragments. The structure of this complex can be described as a dimer of formula $[\text{CuCl}_2(\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2)(\text{CH}_3\text{CN})]_2$ in which the $\text{CH}_3\text{-Pz-COOCH}_2\text{CH}_3$ ligand is coordinated in a bidentate way and remains protonated. The copper atom has a distorted octahedral coordination environment formed by three chlorine atoms, one nitrogen atom of the acetonitrile molecule and two atoms of the unsymmetrical pyrazole ligand – the pyridine-like N1 atom and atom O 1 of the ester substituent in position 3 of the pyrazole ring. The bidentate coordination of the pyrazole ligand leads to the formation of a five-membered chelate ring. The atoms in the ring deviate only slightly from planarity [the Cu1 atom is out of the Cu1/N1/C4/C5/O1 plane by 0.0222 (8) Å; N1 by –0.0406 (14) Å; C4 by 0.0326 (15) Å; C5 by 0.0031 (18) Å and O1 by –0.0172 (14) Å]. Both the copper atoms and the bridging chlorine atoms lie in the same plane without deviations from planarity. The intermetallic distance in the dimer unit is 3.8002 (7) Å while the chlorine–chlorine separation in the four-membered bimetallic cycle is 3.5894 (15) Å.

An overlay of the asymmetric units of the structures of the title compound (red) and a similar complex with methyl 5-methyl-1*H*-pyrazole-3-carboxylate (green) is presented in Fig. 2. The structures were compared using *OLEX2* software (Dolomanov *et al.*, 2009). It was found that the structure of the complex does not change regardless of the organic radical *R* in the COOR ester group, whether $-\text{CH}_3$ or $-\text{CH}_2-\text{CH}_3$. The crystal structures of these compounds are also similar. In addition, the intermetallic distance in the above structures differs approximately by 0.1 Å and the chlorine–chlorine separation in the four-membered bimetallic ring differs by 0.05 Å [$\text{Cu}\cdots\text{Cu} = 3.7047$ (7) Å and $\text{Cl}\cdots\text{Cl} = 3.5364$ (11) Å for the methyl analogue]. The molecular structure is stabilized by intramolecular $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds (Table 1).

3. Supramolecular features

The crystal packing of the title compound (Fig. 3) consists of discrete binuclear molecules with a $\{\text{Cu}_2(\mu_2\text{-Cl})_2\}$ core, which

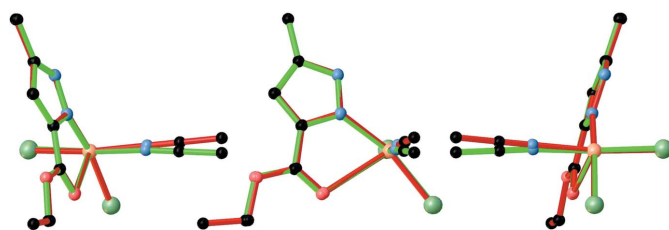


Figure 2
Overlay diagram of the asymmetric units of the structures of the title compound (red) and of a similar complex with methyl 5-methyl-1*H*-pyrazole-3-carboxylate (green) which shows the similarity of the structure regardless of the organic radical *R* in the COOR ester group of the substituent on the pyrazole ring.

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots Cl1^i$	0.80 (2)	2.72 (2)	3.281 (2)	129 (2)
$N2-H2\cdots Cl2^i$	0.80 (2)	2.59 (2)	3.273 (2)	145 (1)
$C7-H7A\cdots Cl2^{ii}$	0.96	2.79	3.662 (4)	151

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

form a planar bimetallic ring. The four-membered $Cu1/Cl1/Cu1^i/Cl1^i$ planes of the bimetallic rings are situated perpendicular to the b axis, while the chelate ring planes are located approximately parallel. No intermolecular hydrogen bonds were identified in the crystal structure. The minimum separation between the Cl atoms of neighbouring molecules inside one unit cell is 4.4013 (13) \AA for $Cl1^i$ and $Cl1^{ii}$ [symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $x, y, -1 + z$] while the minimum distance between two copper atoms is 7.6498 (3) \AA for $Cu1$ and $Cu1^{ii}$.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were performed using *Crystal Explorer 17.5* (Turner *et al.*, 2018), with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed colour scale of -0.1996 (red) to 1.1926 (blue) a.u. The pale-red spots in Fig. 4 represent short contacts and negative d_{norm} values on the surface corresponding to the interactions described above. The Hirshfeld surfaces mapped over d_{norm} are shown for the $H\cdots H$, $H\cdots Cl/Cl\cdots H$, $H\cdots O/O\cdots H$, $H\cdots C/C\cdots H$ and $H\cdots N/N\cdots H$ contacts, the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Fig. 5. Twelve short interatomic contacts in the range 2.34–2.8 \AA are indicated by

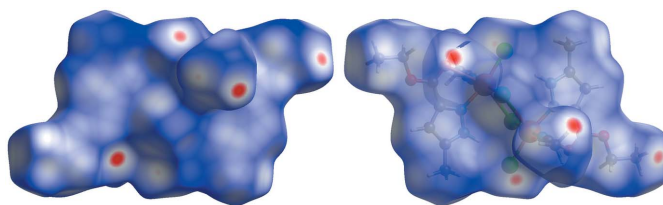


Figure 4

Two projections of Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule.

the faint red spots. Two pairs of intermolecular $C-H\cdots O$ contacts between the O1 atom of the ester substituent and the hydrogen atom of the methyl group of the coordinated acetonitrile were the shortest. Also, four intermolecular $C-H\cdots Cl$ contacts with a length of 2.685 \AA , which are present between the terminal chlorine atoms and the hydrogen atoms of the ethyl group (hydrogen atom near C7) of the ester substituent are also short. Finally, four intermolecular $C-H\cdots Cl$ contacts with a length of 2.8 \AA are observed between the terminal chlorine atoms and the hydrogen atoms of the $-CH_3$ group of the acetonitrile molecule. For the title compound, the most significant contributions to the overall crystal packing are from $H\cdots H$ (40%), $H\cdots Cl/Cl\cdots H$ (24.3%), $H\cdots O/O\cdots H$ (11.8%), $H\cdots C/C\cdots H$ (9.2%) and $H\cdots N/N\cdots H$ (8.3%) contacts. The small contribution of the other weak intermolecular $C\cdots C$ (2.9%), $C\cdots O/O\cdots C$ (2.1%), $C\cdots N/N\cdots C$ (0.8%), $C\cdots Cl/Cl\cdots C$ (0.3%), $O\cdots N/N\cdots O$ (0.3%) and $Cl\cdots Cl$ (0.1%) contacts has a negligible effect on the packing. In addition, quantitative physical properties of the Hirshfeld surface for the title compound were obtained, such as molecular volume (657.89 \AA^3), surface area (571.56 \AA^2), globularity (0.640), as well as asphericity (0.147).

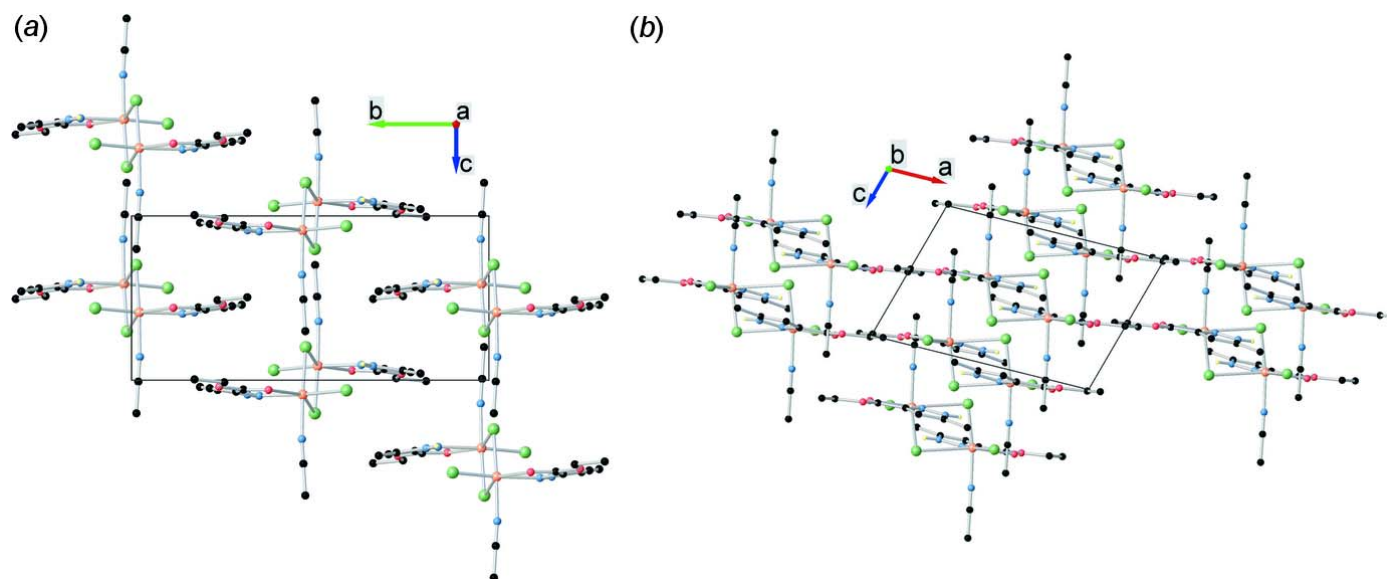


Figure 3

Crystal packing of the title compound viewed along (a) the a - and (b) the b -axis directions. Selected hydrogen atoms were omitted for clarity.

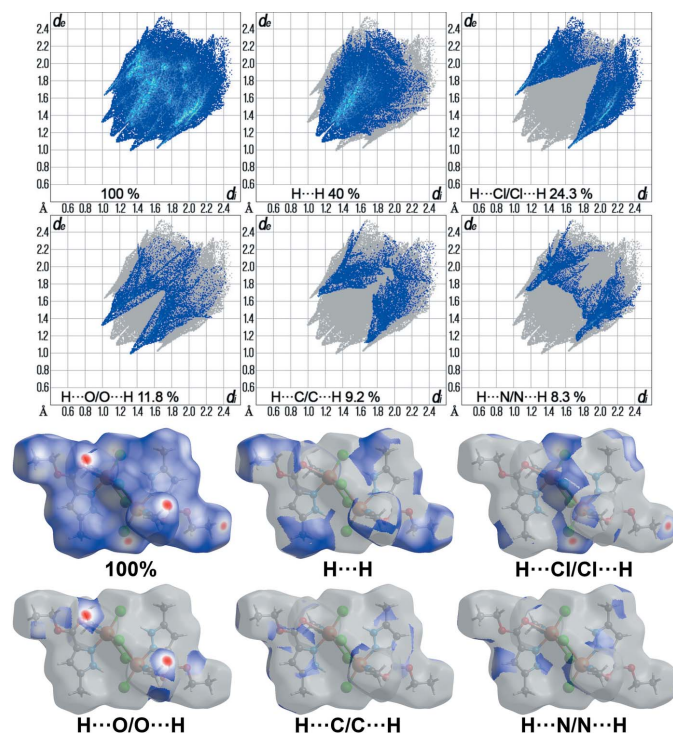


Figure 5
The overall two-dimensional fingerprint plot and those delineated into specified interactions. Hirshfeld surface representations with the function d_{norm} plotted onto the surface for the different interactions.

5. Database survey

Six similar structures are registered in the Cambridge Structural Database (Version 2021.1; Groom *et al.*, 2016): two reports of complexes with methyl 5-methyl-1*H*-pyrazole-3-carboxylate [UMUXEI (Rheingold, 2021) and ZEQUZ (Shakirova *et al.*, 2012)], two reports of the free ligand ethyl 5-methyl-1*H*-pyrazole-3-carboxylate [FAQSAR01 (Mague *et al.*, 2018) and FAQSAR02 (Kusakiewicz-Dawid *et al.*, 2019)] and two structure reports of the same ligand with a different name and cell parameters (Elguero *et al.*, 1999) [3-ethoxycarbonyl-5-methylpyrazole (FAQSAR) and 4-bromo-3-ethoxycarbonyl-5-methylpyrazole (FAQTAS)].

6. Synthesis and crystallization

$[\text{Cu}_2(\mu_2\text{-Cl})_2(\text{CH}_3\text{-Pz-COOCH}_2\text{CH}_3)_2\text{Cl}_2(\text{CH}_3\text{CN})_2]$ was synthesized at room temperature by the oxidative dissolution method by the addition of a copper powder (1.56 mmol, 0.1 g) and copper(II) chloride dihydrate (3.1 mmol, 0.53 g) mixture to an acetonitrile (9 ml) solution of ethyl 5-methyl-1*H*-pyrazole-3-carboxylate (4.67 mmol, 0.72 g). The mixture was stirred without heating for three h with free air access until dissolution of the copper powder and a green precipitate of the product was obtained. The precipitate was filtered off and re-dissolved in acetonitrile. Green crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. The IR spectra of the starting pyrazole ligand and the obtained

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}_2\text{Cl}_4(\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2)_2(\text{C}_2\text{H}_3\text{N})_2]$
M_r	659.33
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	11.3934 (4), 15.9822 (5), 7.6498 (3)
β (°)	106.226 (4)
V (Å ³)	1337.48 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.03
Crystal size (mm)	0.45 × 0.2 × 0.1
Data collection	
Diffractometer	Rigaku Xcalibur, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)
$T_{\text{min}}, T_{\text{max}}$	0.839, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9132, 3062, 2380
R_{int}	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.083, 1.04
No. of reflections	3062
No. of parameters	158
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.30, -0.34

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXL* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

green crystals of the title coordination compound are given in the supporting information.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically (C–H = 0.93–0.97) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C-methyl})$. N-bound H atoms were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXL* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Di- μ -chlorido-bis[(acetonitrile- κ N)chlorido(ethyl 5-methyl-1*H*-pyrazole-3-carboxylate- κ^2 N²,O)copper(II)]

Crystal data

[Cu₂Cl₄(C₅H₁₀N₂O₂)₂(C₂H₃N)₂]
 $M_r = 659.33$
 Monoclinic, $P2_1/c$
 $a = 11.3934$ (4) Å
 $b = 15.9822$ (5) Å
 $c = 7.6498$ (3) Å
 $\beta = 106.226$ (4)°
 $V = 1337.48$ (9) Å³
 $Z = 2$

$F(000) = 668$
 $D_x = 1.637$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3607 reflections
 $\theta = 2.3$ – 27.2 °
 $\mu = 2.03$ mm⁻¹
 $T = 293$ K
 Block, green
 $0.45 \times 0.2 \times 0.1$ mm

Data collection

Rigaku Xcalibur, Eos
 diffractometer
 Radiation source: fine-focus sealed X-ray tube,
 Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.1593 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2021)

$T_{\min} = 0.839$, $T_{\max} = 1.000$
 9132 measured reflections
 3062 independent reflections
 2380 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 28.3$ °, $\theta_{\min} = 1.9$ °
 $h = -14 \rightarrow 14$
 $k = -18 \rightarrow 21$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.083$
 $S = 1.04$

3062 reflections
 158 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.250P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$

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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.32946 (3)	0.47882 (2)	0.91290 (4)	0.03655 (12)
Cl1	0.45100 (6)	0.48716 (4)	1.20189 (9)	0.04438 (18)
Cl2	0.23810 (6)	0.60138 (4)	0.93837 (10)	0.04752 (19)
O1	0.14691 (18)	0.38325 (11)	0.9411 (3)	0.0501 (5)
O2	0.12145 (16)	0.24499 (11)	0.9610 (3)	0.0471 (5)
N1	0.37558 (18)	0.35720 (12)	0.9058 (3)	0.0359 (5)
N2	0.4841 (2)	0.32429 (13)	0.9131 (3)	0.0406 (6)
H2	0.541 (2)	0.3509 (10)	0.9021 (5)	0.049*
N3	0.2412 (2)	0.47671 (13)	0.6418 (3)	0.0452 (6)
C1	0.4879 (2)	0.24100 (15)	0.9412 (4)	0.0414 (7)
C2	0.6021 (3)	0.19159 (18)	0.9591 (5)	0.0628 (10)
H2A	0.624715	0.194792	0.847440	0.094*
H2B	0.588090	0.134232	0.984660	0.094*
H2C	0.666779	0.214025	1.056683	0.094*
C3	0.3747 (2)	0.21906 (15)	0.9510 (4)	0.0417 (6)
H3	0.347635	0.165569	0.967998	0.050*
C4	0.3075 (2)	0.29279 (15)	0.9307 (3)	0.0356 (6)
C5	0.1848 (2)	0.31277 (16)	0.9433 (4)	0.0375 (6)
C6	0.0021 (2)	0.2595 (2)	0.9877 (4)	0.0567 (8)
H6A	-0.049565	0.289751	0.884815	0.068*
H6B	0.009748	0.292321	1.096964	0.068*
C7	-0.0522 (3)	0.1761 (2)	1.0052 (5)	0.0624 (9)
H7A	-0.071569	0.147755	0.890001	0.094*
H7B	-0.125387	0.183416	1.042309	0.094*
H7C	0.005383	0.143312	1.094653	0.094*
C8	0.1955 (3)	0.48097 (15)	0.4916 (4)	0.0417 (6)
C9	0.1373 (4)	0.4863 (2)	0.2988 (4)	0.0710 (10)
H9A	0.150266	0.435166	0.241128	0.107*
H9B	0.171560	0.532163	0.248413	0.107*
H9C	0.051142	0.495250	0.278268	0.107*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0379 (2)	0.03067 (19)	0.0376 (2)	0.00332 (12)	0.00486 (14)	-0.00063 (12)

C11	0.0504 (4)	0.0426 (4)	0.0359 (4)	0.0007 (3)	0.0049 (3)	0.0039 (3)
C12	0.0448 (4)	0.0378 (4)	0.0559 (5)	0.0095 (3)	0.0074 (3)	-0.0022 (3)
O1	0.0491 (12)	0.0414 (11)	0.0637 (14)	0.0052 (9)	0.0224 (10)	-0.0034 (9)
O2	0.0351 (10)	0.0452 (11)	0.0642 (14)	-0.0029 (8)	0.0190 (9)	0.0025 (9)
N1	0.0305 (11)	0.0312 (11)	0.0449 (14)	-0.0011 (9)	0.0088 (10)	-0.0021 (9)
N2	0.0329 (12)	0.0353 (12)	0.0544 (16)	-0.0048 (9)	0.0133 (11)	-0.0057 (10)
N3	0.0471 (14)	0.0425 (13)	0.0431 (15)	0.0053 (10)	0.0077 (12)	-0.0029 (10)
C1	0.0382 (15)	0.0301 (13)	0.0526 (18)	0.0006 (11)	0.0074 (13)	-0.0075 (11)
C2	0.0442 (17)	0.0463 (17)	0.094 (3)	0.0062 (13)	0.0121 (18)	-0.0150 (16)
C3	0.0399 (15)	0.0311 (13)	0.0517 (18)	-0.0041 (11)	0.0085 (13)	-0.0003 (11)
C4	0.0338 (13)	0.0329 (13)	0.0382 (16)	-0.0032 (10)	0.0069 (11)	-0.0037 (10)
C5	0.0370 (14)	0.0385 (15)	0.0368 (16)	-0.0040 (11)	0.0101 (12)	-0.0034 (11)
C6	0.0422 (17)	0.073 (2)	0.059 (2)	0.0066 (14)	0.0209 (16)	0.0057 (16)
C7	0.0416 (17)	0.084 (2)	0.062 (2)	-0.0189 (15)	0.0156 (16)	-0.0033 (17)
C8	0.0464 (16)	0.0391 (15)	0.0406 (18)	0.0057 (11)	0.0136 (13)	-0.0044 (11)
C9	0.090 (3)	0.083 (2)	0.038 (2)	0.0103 (19)	0.0133 (19)	-0.0022 (16)

Geometric parameters (Å, °)

Cu1—Cl1 ⁱ	2.9242 (8)	C2—H2A	0.9600
Cu1—Cl1	2.2609 (7)	C2—H2B	0.9600
Cu1—Cl2	2.2521 (7)	C2—H2C	0.9600
Cu1—O1	2.637 (2)	C3—H3	0.9300
Cu1—N1	2.0182 (19)	C3—C4	1.390 (3)
Cu1—N3	2.036 (2)	C4—C5	1.462 (4)
O1—C5	1.205 (3)	C6—H6A	0.9700
O2—C5	1.330 (3)	C6—H6B	0.9700
O2—C6	1.449 (3)	C6—C7	1.492 (4)
N1—N2	1.330 (3)	C7—H7A	0.9600
N1—C4	1.335 (3)	C7—H7B	0.9600
N2—H2	0.80 (3)	C7—H7C	0.9600
N2—C1	1.347 (3)	C8—C9	1.441 (4)
N3—C8	1.123 (4)	C9—H9A	0.9600
C1—C2	1.495 (4)	C9—H9B	0.9600
C1—C3	1.360 (4)	C9—H9C	0.9600
Cl1—Cu1—Cl1 ⁱ	86.62 (3)	H2A—C2—H2C	109.5
Cl1—Cu1—O1	103.64 (5)	H2B—C2—H2C	109.5
Cl2—Cu1—Cl1	92.05 (3)	C1—C3—H3	127.0
Cl2—Cu1—Cl1 ⁱ	108.61 (3)	C1—C3—C4	106.1 (2)
Cl2—Cu1—O1	95.89 (5)	C4—C3—H3	127.0
O1—Cu1—Cl1 ⁱ	153.19 (4)	N1—C4—C3	110.2 (2)
N1—Cu1—Cl1	89.44 (6)	N1—C4—C5	116.5 (2)
N1—Cu1—Cl1 ⁱ	85.41 (6)	C3—C4—C5	133.2 (2)
N1—Cu1—Cl2	165.96 (7)	O1—C5—O2	124.1 (2)
N1—Cu1—O1	70.22 (7)	O1—C5—C4	123.3 (2)
N1—Cu1—N3	90.84 (8)	O2—C5—C4	112.6 (2)
N3—Cu1—Cl1	171.83 (7)	O2—C6—H6A	110.2

N3—Cu1—C11 ⁱ	85.27 (7)	O2—C6—H6B	110.2
N3—Cu1—C12	89.66 (6)	O2—C6—C7	107.4 (2)
N3—Cu1—O1	84.12 (8)	H6A—C6—H6B	108.5
C5—O1—Cu1	104.76 (17)	C7—C6—H6A	110.2
C5—O2—C6	116.2 (2)	C7—C6—H6B	110.2
N2—N1—Cu1	128.73 (16)	C6—C7—H7A	109.5
N2—N1—C4	105.05 (19)	C6—C7—H7B	109.5
C4—N1—Cu1	124.95 (17)	C6—C7—H7C	109.5
N1—N2—H2	123.6	H7A—C7—H7B	109.5
N1—N2—C1	112.7 (2)	H7A—C7—H7C	109.5
C1—N2—H2	123.6	H7B—C7—H7C	109.5
C8—N3—Cu1	175.2 (2)	N3—C8—C9	179.8 (4)
N2—C1—C2	121.7 (2)	C8—C9—H9A	109.5
N2—C1—C3	105.9 (2)	C8—C9—H9B	109.5
C3—C1—C2	132.4 (2)	C8—C9—H9C	109.5
C1—C2—H2A	109.5	H9A—C9—H9B	109.5
C1—C2—H2B	109.5	H9A—C9—H9C	109.5
C1—C2—H2C	109.5	H9B—C9—H9C	109.5
H2A—C2—H2B	109.5		
Cu1—O1—C5—O2	178.2 (2)	N2—C1—C3—C4	-1.0 (3)
Cu1—O1—C5—C4	-0.4 (3)	C1—C3—C4—N1	1.1 (3)
Cu1—N1—N2—C1	167.66 (19)	C1—C3—C4—C5	-174.1 (3)
Cu1—N1—C4—C3	-168.89 (18)	C2—C1—C3—C4	177.7 (3)
Cu1—N1—C4—C5	7.2 (3)	C3—C4—C5—O1	171.4 (3)
N1—N2—C1—C2	-178.3 (3)	C3—C4—C5—O2	-7.4 (4)
N1—N2—C1—C3	0.5 (3)	C4—N1—N2—C1	0.2 (3)
N1—C4—C5—O1	-3.7 (4)	C5—O2—C6—C7	-179.7 (2)
N1—C4—C5—O2	177.6 (2)	C6—O2—C5—O1	-3.1 (4)
N2—N1—C4—C3	-0.8 (3)	C6—O2—C5—C4	175.7 (2)
N2—N1—C4—C5	175.3 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots C11 ⁱ	0.80 (2)	2.72 (2)	3.281 (2)	129 (2)
N2—H2 \cdots C12 ⁱ	0.80 (2)	2.59 (2)	3.273 (2)	145 (1)
C7—H7A \cdots C12 ⁱⁱ	0.96	2.79	3.662 (4)	151

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