



# Crystal structure and Hirshfeld surface analysis of a new polymorph of chloridobis(1,10-phenanthroline- $\kappa^2N,N'$ )copper(II) perchlorate

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Received 20 November 2024

Accepted 9 January 2025

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords:** copper; copper(II) complex; crystal structure; 1,10-phenanthroline; Hirshfeld surface analysis.

**CCDC reference:** 2415829

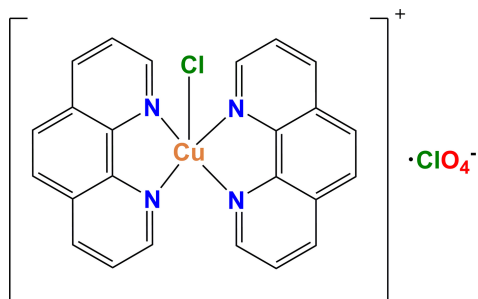
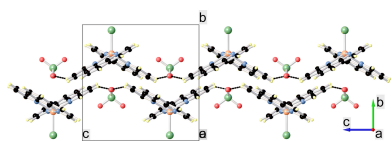
**Supporting information:** this article has supporting information at journals.iucr.org/e

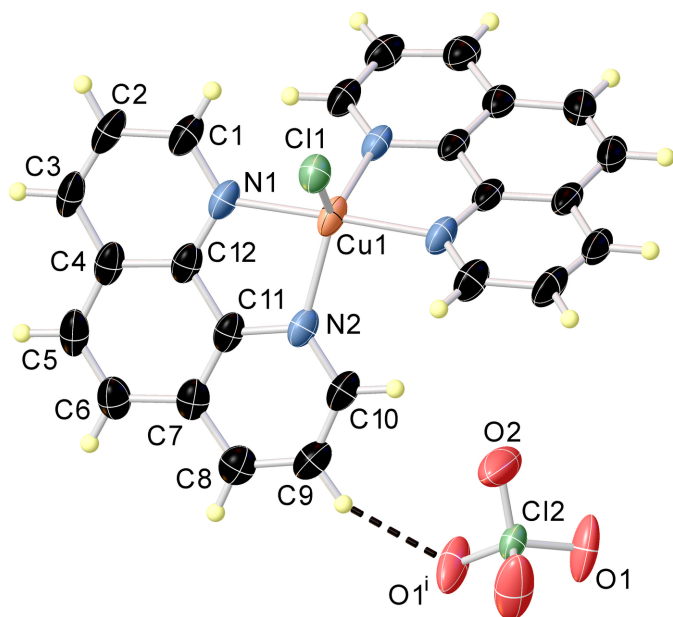
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The title salt (systematic name: 2-methyl-4-oxo-3,4-dihydroquinazolin-1-ium chloride),  $[\text{CuCl}(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{ClO}_4)$ , is comprised of a mononuclear complex cation  $[\text{Cu}(\text{phen})_2\text{Cl}]^+$  (phen is 1,10-phenanthroline) and a perchlorate anion,  $\text{ClO}_4^-$ , both with point group symmetry 2. The  $\text{Cu}^{\text{II}}$  atom has a slightly distorted trigonal–bipyramidal coordination environment, defined by a  $\text{N}_4\text{Cl}$  coordination set with the Cl atom and two N atoms at the equatorial sites. In the crystal, each phen ring is parallel to neighboring phen rings. The resulting significant  $\pi$ – $\pi$  stacking interactions lead to zigzag chains extending parallel to [001]. Hirshfeld surface analysis suggests that the most important contributions to the surface contacts are from  $\text{H}\cdots\text{H}$  (32.1%),  $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$  (18.2%),  $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$  (14.6%),  $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$  (12.7%) and  $\text{C}\cdots\text{C}$  (10.6%) interactions.

## 1. Chemical context

1,10-Phenanthroline (phen) is one of the most extensively studied chelating N-heterocyclic ligands. Copper(II) complexes of phen, particularly those exhibiting a coordination environment with coordination number 5, have garnered significant attention due to their diverse biological (Barceló-Oliver *et al.*, 2009; Pradeep *et al.*, 2014), redox catalytic (Huang & Batey, 2007; Liu *et al.*, 2024), and photochemical (Freitag *et al.*, 2016) activities. Furthermore, complexes formed between copper and phen (in both 1:1 and 1:2 metal-to-ligand ratios) have been actively investigated as DNA-binding and oxidative DNA-cleaving agents (Bales *et al.*, 2005; Zhang *et al.*, 2006; Pradeep *et al.*, 2014). In this context, structural studies of five-coordinate  $\text{Cu}^{\text{II}}$  complexes based on phen are of considerable interest for enhancing the understanding of the geometric features of the  $\text{CuN}_4\text{X}$  chromophore and for elucidating the structure–property relationships of these compounds.



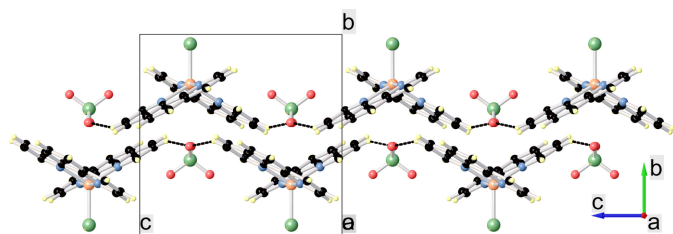


**Figure 1**  
The structures of the molecular entities of the title compound. Displacement ellipsoids are drawn at the 50% probability level. The dashed line represents a C—H···O hydrogen bond. [Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .]

Here, we report on synthesis, crystal structure, and Hirshfeld surface analysis of the compound  $[\text{CuCl}(\text{phen})_2]\text{ClO}_4$ , crystallizing as a novel polymorph.

## 2. Structural commentary

The asymmetric unit of the title compound consists of half a  $[\text{Cu}(\text{phen})_2\text{Cl}]^+$  complex cation (point group symmetry 2) and half of a perchlorate anion  $\text{ClO}_4^-$  (point group symmetry 2). The  $\text{Cu}^{\text{II}}$  ion in the complex cation has a slightly distorted trigonal-bipyramidal coordination environment ( $\tau_5 = 0.921$ ; Addison *et al.*, 1984) formed by four nitrogen atoms from two phen ligands and one  $\text{Cl}^-$  ligand (Fig. 1). The equatorial plane is defined by atoms Cl1, N1 and N1<sup>i</sup> whereas the axial positions are occupied by atoms N2 and N2<sup>i</sup> [symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ ]. The Cu—N bond lengths to the equatorial N atoms are shorter by about 0.11 Å in comparison to the axial N atoms (Table 1). The crystallographically unique phen



**Figure 2**  
Packing of the molecular components in the title compound in a view along the *a* axis. C—H···O hydrogen bonds are shown as black dashed lines.

**Table 1**  
Selected bond lengths (Å).

Cu1—N1	1.988 (2)	Cl2—O2	1.418 (3)
Cu1—N2	2.100 (2)	Cl2—O1	1.420 (2)
Cu1—Cl1	2.3402 (12)		

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C9—H9···O1 <sup>i</sup>	0.95	2.43	3.253 (4)	145
C3—H3···O2 <sup>ii</sup>	0.95	2.48	3.368 (5)	157

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

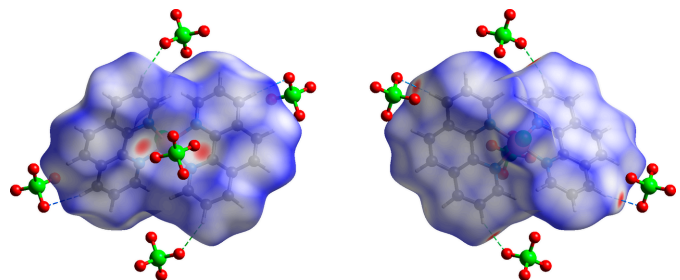
molecule retains its planarity [maximum deviation from the least-squares plane is 0.034 (3) Å for atom C2] and forms a five-membered [Cu—N—C—C—N] chelate ring due to its bidentate coordination. The dihedral angle between the two phen planes coordinating to Cu1 is 59.55 (6)°. The twist angle between the planes is 48.32 (5)°, the fold angle between the planes is 39.10 (8)°, whereby the twist angle refers to the rotation of one phen plane relative to the other, while the fold angle describes the bending between the planes.

## 3. Supramolecular features

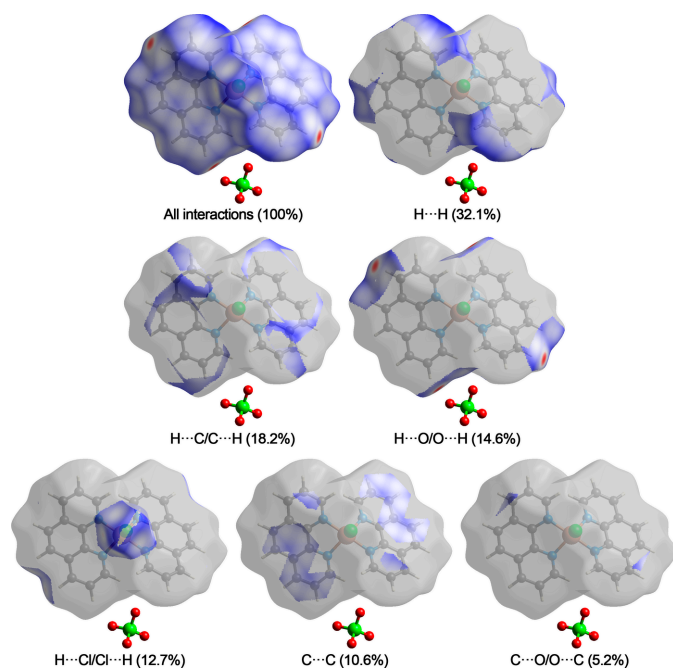
In the crystal structure of the title compound (Fig. 2), each phen ring is parallel to its neighboring phen ring. The resulting significant  $\pi$ — $\pi$  stacking with an inter-planar distance of 3.5085 (16) Å leads to a zigzag chain structure extending parallel to [001]. There are additional weak intermolecular C—H···O hydrogen bonds that link the complex cation to the perchlorate anion. Numerical details of these interactions are compiled in Table 2. The shortest Cu···Cu separation within the unit cell is 7.7779 (3) Å.

## 4. Hirshfeld analysis

Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were generated using *CrystalExplorer* (Spackman *et al.*, 2021). The dark-red spots in Fig. 3 arise as a result of short interatomic contacts and represent negative  $d_{\text{norm}}$  values on the surface, while the other weaker intermolecular interactions appear as light-red spots.

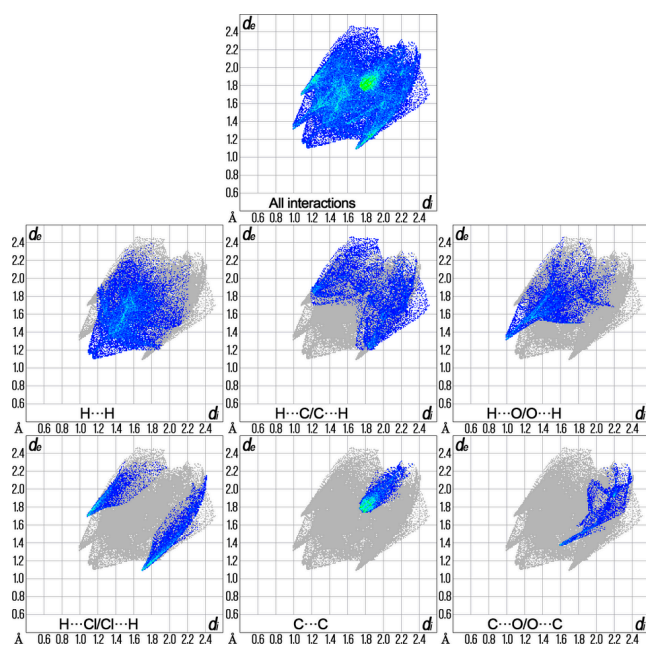


**Figure 3**  
Hirshfeld surface mapped over  $d_{\text{norm}}$  in a projection along the *b* axis (front and back view).



**Figure 4**  
Hirshfeld surface representations with the function  $d_{\text{norm}}$  plotted onto the surface for individual interactions.

The Hirshfeld surfaces mapped over  $d_{\text{norm}}$  are shown individually for the  $\text{H}\cdots\text{H}$ ,  $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ ,  $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ ,  $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ ,  $\text{C}\cdots\text{C}$  and  $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$  contacts (Fig. 4). The overall two-dimensional fingerprint plot and those decomposed into individual contacts are given in Fig. 5. The most significant contributions to the overall crystal packing are from  $\text{H}\cdots\text{H}$



**Figure 5**  
The overall two-dimensional fingerprint plot and those delineated into specified interactions.

(32.1%),  $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$  (18.2%),  $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$  (14.6%),  $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$  (12.7%) and  $\text{C}\cdots\text{C}$  (10.6%) contacts. There are also small contributions from  $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$  (5.2%),  $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$  (2.4%),  $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$  (2.2%),  $\text{O}\cdots\text{N}/\text{N}\cdots\text{O}$  (1.8%) and  $\text{O}\cdots\text{Cl}/\text{Cl}\cdots\text{O}$  (0.3%) intermolecular contacts.

In the context of the Hirshfeld surface analysis, quantitative physical properties for the title compound were obtained, such as molecular volume ( $460.76 \text{ \AA}^3$ ), surface area ( $398.28 \text{ \AA}^2$ ), globularity (0.724) and asphericity (0.097). The asphericity value for the title compound is nearly zero, indicating an almost isotropic nature. The globularity value, being less than one, points to a slight deviation from a spherical shape.

## 5. Database survey

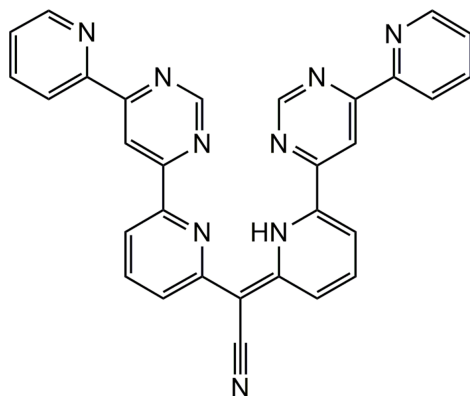
A search conducted in the Cambridge Structural Database (CSD, version 5.44, updated June 2023; Groom *et al.*, 2016) identified a total of 118 entries corresponding to compounds containing the  $[\text{CuCl}(\text{phen})_2]^+$  cation. Among these, five entries specifically pertain to compounds that include both the  $[\text{CuCl}(\text{phen})_2]^+$  cation and the perchlorate anion. Notably, one structure was identified with the same formula as the title compound,  $[\text{CuCl}(\text{phen})_2]\text{ClO}_4$  (CLPLCU, Boys *et al.*, 1981; CLPLCU01, Daizhi *et al.*, 2006), revealing that this compound is at least dimorphic. The other matches have formulas  $[\text{CuCl}(\text{phen})_2]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$  (ASUCOG, Wei & Yang, 2004) and  $[\text{CuCl}(\text{phen})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$  (FUVWUP, Chang *et al.*, 2008; JATRAA, Crispini *et al.*, 2018).

CLPLCU and ASUCOG crystallize in space group  $P2_1/c$ , FUVWUP in  $P2_1/n$  and JATRAA in  $P\bar{1}$ . The cell volumes are  $4490.3 \text{ \AA}^3$  for ASUCOG ( $Z = 8$ ),  $2283.0 \text{ \AA}^3$  for CLPLCU ( $Z = 4$ ),  $2335.18 \text{ \AA}^3$  for FUVWUP ( $Z = 4$ ),  $1185.88 \text{ \AA}^3$  for JATRAA ( $Z = 2$ ), and  $2153.12 \text{ \AA}^3$  for the title compound ( $C2/c$ ,  $Z = 4$ ). Thus, the title compound has the smallest volume per formula unit.

ASUCOG contains two crystallographically unique  $[\text{CuCl}(\text{phen})_2]^+$  cations, while all other structures contain only one crystallographically unique complex cation. In general, bond lengths and angles of the  $[\text{CuCl}(\text{phen})_2]^+$  cation are very similar for all described complexes.  $\text{Cu}-\text{N}$  bond lengths lie in the range  $1.970\text{--}2.135 \text{ \AA}$ , in good agreement with the title complex, whereas  $\text{Cu}-\text{Cl}$  bond lengths ( $2.269\text{--}2.326 \text{ \AA}$ ) are slightly shorter than in the title compound. The crystal structures of all hydrous compounds (ASUCOG, FUVWUP, JATRAA) include  $\text{Cu}-\text{Cl}\cdots\text{HOH}\cdots\text{O}-\text{Cl}$  hydrogen-bond motifs.

## 6. Synthesis and crystallization

The title compound was obtained during an attempt to synthesize a trinuclear complex based on the polypyridyl ligand *L*, which includes one tetradentate and two bidentate metal-binding sites (Fig. 6; Fritsky *et al.*, 2003; Strotmeyer *et al.*, 2003). Copper(II) chloride dihydrate (0.034 g, 0.2 mmol) dissolved in methanol (5 ml) was added to a solution of 1,10-phenanthroline (0.036 g, 0.2 mmol) in methanol (5 ml). Separately,  $[\text{Cu}(\text{L}-\text{H})(\text{MeOH})]\text{ClO}_4$  (0.070 g, 0.1 mmol),



**Figure 6**  
The polypyridyl ligand involved in the synthesis of the title compound.

prepared according to Fritsky *et al.* (2001), was dissolved in a 1:1 (v:v) methanol–water mixture (10 ml). The two solutions were combined, stirred in air for 30 min. while heated (323 K), then cooled, filtered, and left at room temperature for crystallization. X-ray-quality, small green block-like crystals formed after two weeks. Yield: 0.034 g (61 %).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The positions of H atoms were positioned geometrically and refined isotropically using a riding model with C–H = 0.95 Å;  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Funding information

Funding for this research was provided by: the Ministry of Education and Science of Ukraine through grants No. 22BF037-09 and 24DF037-04N (RN/61-2024) .

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**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[CuCl(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> )
$M_r$	558.85
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	120
$a, b, c$ (Å)	15.7143 (5), 11.6386 (4), 13.0138 (5)
$\beta$ (°)	115.227 (2)
$V$ (Å <sup>3</sup> )	2153.12 (13)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.31
Crystal size (mm)	0.13 × 0.13 × 0.09
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.642, 0.880
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	21362, 2471, 1947
$R_{\text{int}}$	0.050
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.105, 1.06
No. of reflections	2471
No. of parameters	160
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.70, -0.57

Computer programs: *COLLECT* (Bruker, 2004), *DENZO/SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2019/2* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *pubCIF* (Westrip, 2010).

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## supporting information

*Acta Cryst.* (2025). E81, 140-143 [https://doi.org/10.1107/S2056989025000209]

## Crystal structure and Hirshfeld surface analysis of a new polymorph of chloridobis(1,10-phenanthroline- $\kappa^2N,N'$ )copper(II) perchlorate

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### Computing details

#### Chloridobis(1,10-phenanthroline- $\kappa^2N,N'$ )copper(II) perchlorate

##### Crystal data

[CuCl(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)

$M_r = 558.85$

Monoclinic, *C2/c*

$a = 15.7143$  (5) Å

$b = 11.6386$  (4) Å

$c = 13.0138$  (5) Å

$\beta = 115.227$  (2)°

$V = 2153.12$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 1132$

$D_x = 1.724$  Mg m<sup>-3</sup>

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

Cell parameters from 1037 reflections

$\theta = 3.1$ – $27.5$ °

$\mu = 1.31$  mm<sup>-1</sup>

$T = 120$  K

Block, green

$0.13 \times 0.13 \times 0.09$  mm

##### Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 9 pixels mm<sup>-1</sup>

$\varphi$  scans and  $\omega$  scans with  $\kappa$  offset

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.642$ ,  $T_{\max} = 0.880$

21362 measured reflections

2471 independent reflections

1947 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 2.3$ °

$h = -20 \rightarrow 20$

$k = -15 \rightarrow 15$

$l = -16 \rightarrow 16$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.105$

$S = 1.06$

2471 reflections

160 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 5.6416P]$

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

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

$\Delta\rho_{\max} = 0.70$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.56$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.000000	0.24858 (4)	0.250000	0.03782 (18)
Cl1	0.000000	0.04751 (9)	0.250000	0.0380 (3)
Cl2	0.000000	0.37251 (8)	-0.250000	0.0303 (2)
O1	0.07641 (18)	0.4406 (2)	-0.2458 (3)	0.0632 (8)
O2	0.0293 (2)	0.3002 (3)	-0.1533 (3)	0.0819 (10)
N1	-0.10679 (18)	0.2549 (2)	0.2935 (2)	0.0364 (6)
N2	-0.09691 (17)	0.33812 (19)	0.1083 (2)	0.0320 (5)
C1	-0.1099 (2)	0.2086 (3)	0.3852 (3)	0.0430 (7)
H1	-0.055627	0.170922	0.439318	0.052*
C2	-0.1913 (2)	0.2140 (3)	0.4040 (3)	0.0438 (8)
H2	-0.191784	0.179833	0.470096	0.053*
C3	-0.2694 (2)	0.2679 (3)	0.3281 (3)	0.0399 (7)
H3	-0.324559	0.271466	0.340803	0.048*
C4	-0.2683 (2)	0.3186 (2)	0.2303 (2)	0.0349 (7)
C5	-0.3467 (2)	0.3764 (3)	0.1452 (3)	0.0415 (7)
H5	-0.403151	0.384501	0.154666	0.050*
C6	-0.3421 (2)	0.4199 (3)	0.0512 (3)	0.0405 (7)
H6	-0.395219	0.458075	-0.004311	0.049*
C7	-0.2578 (2)	0.4090 (2)	0.0343 (3)	0.0343 (6)
C8	-0.2487 (2)	0.4508 (2)	-0.0620 (3)	0.0382 (7)
H8	-0.300060	0.487821	-0.121269	0.046*
C9	-0.1647 (2)	0.4373 (2)	-0.0691 (3)	0.0385 (7)
H9	-0.157107	0.466637	-0.132784	0.046*
C10	-0.0908 (2)	0.3806 (2)	0.0169 (3)	0.0359 (7)
H10	-0.033379	0.371728	0.010016	0.043*
C11	-0.1797 (2)	0.3536 (2)	0.1167 (2)	0.0308 (6)
C12	-0.1844 (2)	0.3084 (2)	0.2167 (2)	0.0320 (6)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0417 (3)	0.0452 (3)	0.0423 (3)	0.000	0.0331 (3)	0.000
Cl1	0.0354 (5)	0.0433 (6)	0.0415 (6)	0.000	0.0222 (5)	0.000
Cl2	0.0319 (5)	0.0321 (5)	0.0365 (5)	0.000	0.0239 (4)	0.000
O1	0.0645 (16)	0.0475 (14)	0.112 (2)	-0.0249 (12)	0.0710 (17)	-0.0274 (14)
O2	0.0681 (18)	0.123 (3)	0.0741 (19)	0.0427 (18)	0.0489 (16)	0.0583 (19)
N1	0.0428 (14)	0.0412 (13)	0.0388 (13)	-0.0026 (11)	0.0303 (12)	-0.0019 (11)
N2	0.0399 (13)	0.0307 (12)	0.0373 (13)	-0.0015 (10)	0.0278 (11)	-0.0046 (10)
C1	0.0514 (19)	0.0477 (17)	0.0452 (18)	-0.0009 (15)	0.0352 (16)	0.0023 (14)

C2	0.057 (2)	0.0477 (17)	0.0468 (18)	-0.0089 (15)	0.0414 (17)	-0.0061 (15)
C3	0.0404 (17)	0.0485 (18)	0.0453 (17)	-0.0152 (14)	0.0321 (15)	-0.0160 (14)
C4	0.0384 (16)	0.0372 (15)	0.0397 (16)	-0.0130 (12)	0.0269 (14)	-0.0174 (13)
C5	0.0330 (15)	0.0512 (18)	0.0486 (18)	-0.0122 (13)	0.0254 (14)	-0.0187 (15)
C6	0.0333 (15)	0.0471 (18)	0.0437 (18)	-0.0033 (13)	0.0190 (14)	-0.0113 (14)
C7	0.0367 (15)	0.0327 (14)	0.0389 (16)	-0.0083 (12)	0.0211 (13)	-0.0129 (12)
C8	0.0434 (17)	0.0359 (15)	0.0383 (17)	-0.0038 (13)	0.0202 (14)	-0.0067 (12)
C9	0.0538 (19)	0.0337 (15)	0.0377 (16)	-0.0058 (14)	0.0288 (15)	-0.0025 (13)
C10	0.0455 (17)	0.0347 (15)	0.0403 (16)	-0.0030 (13)	0.0305 (14)	-0.0028 (12)
C11	0.0383 (15)	0.0281 (13)	0.0355 (15)	-0.0089 (11)	0.0248 (13)	-0.0122 (11)
C12	0.0383 (15)	0.0312 (14)	0.0357 (15)	-0.0089 (12)	0.0246 (13)	-0.0116 (12)

*Geometric parameters (Å, °)*

Cu1—N1	1.988 (2)	C3—C4	1.409 (4)
Cu1—N1 <sup>i</sup>	1.988 (2)	C3—H3	0.9500
Cu1—N2 <sup>i</sup>	2.100 (2)	C4—C12	1.408 (4)
Cu1—N2	2.100 (2)	C4—C5	1.426 (5)
Cu1—C11	2.3402 (12)	C5—C6	1.355 (5)
Cl2—O2 <sup>ii</sup>	1.418 (3)	C5—H5	0.9500
Cl2—O2	1.418 (3)	C6—C7	1.438 (4)
Cl2—O1	1.420 (2)	C6—H6	0.9500
Cl2—O1 <sup>ii</sup>	1.420 (2)	C7—C11	1.397 (4)
N1—C1	1.330 (4)	C7—C8	1.406 (4)
N1—C12	1.354 (4)	C8—C9	1.370 (4)
N2—C10	1.329 (3)	C8—H8	0.9500
N2—C11	1.363 (3)	C9—C10	1.389 (4)
C1—C2	1.403 (4)	C9—H9	0.9500
C1—H1	0.9500	C10—H10	0.9500
C2—C3	1.358 (5)	C11—C12	1.435 (4)
C2—H2	0.9500		
N1—Cu1—N1 <sup>i</sup>	175.73 (14)	C2—C3—H3	120.1
N1—Cu1—N2 <sup>i</sup>	96.66 (9)	C4—C3—H3	120.1
N1 <sup>i</sup> —Cu1—N2 <sup>i</sup>	81.20 (9)	C12—C4—C3	116.8 (3)
N1—Cu1—N2	81.20 (9)	C12—C4—C5	119.2 (3)
N1 <sup>i</sup> —Cu1—N2	96.66 (9)	C3—C4—C5	124.0 (3)
N2 <sup>i</sup> —Cu1—N2	120.50 (12)	C6—C5—C4	121.0 (3)
N1—Cu1—C11	92.13 (7)	C6—C5—H5	119.5
N1 <sup>i</sup> —Cu1—C11	92.13 (7)	C4—C5—H5	119.5
N2 <sup>i</sup> —Cu1—C11	119.75 (6)	C5—C6—C7	120.9 (3)
N2—Cu1—C11	119.75 (6)	C5—C6—H6	119.6
O2 <sup>ii</sup> —Cl2—O2	107.1 (3)	C7—C6—H6	119.6
O2 <sup>ii</sup> —Cl2—O1	108.37 (15)	C11—C7—C8	117.0 (3)
O2—Cl2—O1	110.36 (19)	C11—C7—C6	119.2 (3)
O2 <sup>ii</sup> —Cl2—O1 <sup>ii</sup>	110.36 (19)	C8—C7—C6	123.8 (3)
O2—Cl2—O1 <sup>ii</sup>	108.37 (15)	C9—C8—C7	119.2 (3)
O1—Cl2—O1 <sup>ii</sup>	112.1 (2)	C9—C8—H8	120.4

C1—N1—C12	118.9 (3)	C7—C8—H8	120.4
C1—N1—Cu1	126.8 (2)	C8—C9—C10	119.9 (3)
C12—N1—Cu1	114.29 (18)	C8—C9—H9	120.1
C10—N2—C11	117.2 (3)	C10—C9—H9	120.1
C10—N2—Cu1	132.0 (2)	N2—C10—C9	122.9 (3)
C11—N2—Cu1	110.81 (18)	N2—C10—H10	118.5
N1—C1—C2	121.6 (3)	C9—C10—H10	118.5
N1—C1—H1	119.2	N2—C11—C7	123.8 (2)
C2—C1—H1	119.2	N2—C11—C12	116.4 (3)
C3—C2—C1	120.2 (3)	C7—C11—C12	119.9 (2)
C3—C2—H2	119.9	N1—C12—C4	122.9 (3)
C1—C2—H2	119.9	N1—C12—C11	117.3 (2)
C2—C3—C4	119.7 (3)	C4—C12—C11	119.8 (3)
C12—N1—C1—C2	0.0 (5)	C10—N2—C11—C12	-179.2 (2)
Cu1—N1—C1—C2	-176.8 (2)	Cu1—N2—C11—C12	0.4 (3)
N1—C1—C2—C3	-0.3 (5)	C8—C7—C11—N2	-0.2 (4)
C1—C2—C3—C4	-0.1 (5)	C6—C7—C11—N2	179.5 (2)
C2—C3—C4—C12	0.8 (4)	C8—C7—C11—C12	-179.7 (2)
C2—C3—C4—C5	179.5 (3)	C6—C7—C11—C12	0.0 (4)
C12—C4—C5—C6	1.0 (4)	C1—N1—C12—C4	0.8 (4)
C3—C4—C5—C6	-177.7 (3)	Cu1—N1—C12—C4	178.0 (2)
C4—C5—C6—C7	0.0 (5)	C1—N1—C12—C11	-177.7 (3)
C5—C6—C7—C11	-0.5 (4)	Cu1—N1—C12—C11	-0.5 (3)
C5—C6—C7—C8	179.1 (3)	C3—C4—C12—N1	-1.2 (4)
C11—C7—C8—C9	-1.2 (4)	C5—C4—C12—N1	180.0 (3)
C6—C7—C8—C9	179.2 (3)	C3—C4—C12—C11	177.3 (2)
C7—C8—C9—C10	1.5 (4)	C5—C4—C12—C11	-1.5 (4)
C11—N2—C10—C9	-1.0 (4)	N2—C11—C12—N1	0.1 (4)
Cu1—N2—C10—C9	179.5 (2)	C7—C11—C12—N1	179.6 (2)
C8—C9—C10—N2	-0.4 (4)	N2—C11—C12—C4	-178.5 (2)
C10—N2—C11—C7	1.3 (4)	C7—C11—C12—C4	1.0 (4)
Cu1—N2—C11—C7	-179.1 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9 $\cdots$ O1 <sup>ii</sup>	0.95	2.43	3.253 (4)	145
C3—H3 $\cdots$ O2 <sup>iii</sup>	0.95	2.48	3.368 (5)	157

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