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Poly[[chlorido(1,10-phenanthroline- κ^2N,N')copper(II)]- μ_3 -1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa^3N:N':N''$]: coordination polymer sheets linked into bilayers by hydrogen bonds

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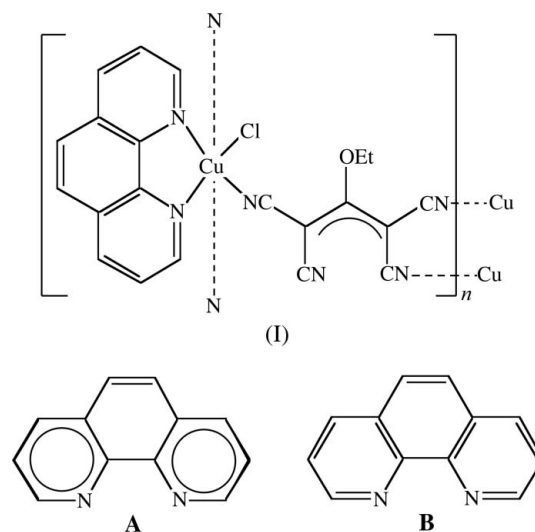
In the title compound, $[\text{Cu}(\text{C}_9\text{H}_5\text{N}_4\text{O})\text{Cl}(\text{C}_{12}\text{H}_8\text{N}_2)]_n$ or $[\text{Cu}(\text{tcnoet})\text{Cl}(\text{phen})]_n$, where phen is 1,10-phenanthroline and tcnoet is 1,1,3,3-tetracyano-2-ethoxypropenide, the axially elongated (4 + 2) coordination polyhedron around the Cu^{II} centre contains N atoms from three different tcnoet ligands. The resulting coordination polymer takes the form of sheets which are linked in pairs by a single $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond to form bilayers. The bond lengths provide evidence for significant bond fixation in the phen ligand and extensive electronic delocalization in the tcnoet ligand, where the two $-\text{C}(\text{CN})_2$ units are rotated, in conrotatory fashion, out of the plane of the central C_3O fragment.

Keywords: crystal structure; coordination polymer; hydrogen bonding; anionic polynitrile ligands; tcnoet ligands; 1,1,3,3-tetracyano-2-ethoxypropenide; (4+2) coordination polyhedron; copper complex.

1. Introduction

We report here the structure of the title compound, poly[[chlorido(1,10-phenanthroline- κ^2N,N')copper(II)]- μ_3 -1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa^3N:N':N''$], (I) (Fig. 1),

which was crystallized from a solution in aqueous ethanol containing equimolar quantities of 1,10-phenanthroline, potassium 1,1,3,3-tetracyano-2-ethoxypropenide and copper(II) chloride dihydrate. Anionic polynitrile ligands are of interest because of their ability to act as bridging ligands, generating a range of different topologies in one, two or three dimensions, either with or without the presence of other co-ligands (Thétiot *et al.*, 2003; Batten *et al.*, 1998, 1999, 2000; Setifi *et al.*, 2006, 2007, 2009, 2010). Compound (I) is an example in which there are two different co-ligands, one each of 1,10-phenanthroline and chloride, alongside the polynitrile ligand, and where the resulting coordination polymer is two-dimensional.



Scheme 1

2. Experimental

2.1. Synthesis and crystallization

The salt $\text{K}(\text{tcnoet})$ was prepared according to the published method of Middleton *et al.* (1958). For the synthesis of compound (I), solutions containing 1,10-phenanthroline (1 mmol) in ethanol (10 ml) and $\text{K}(\text{tcnoet})$ (1 mmol) in water (5 ml) were mixed, and then a solution containing copper(II) chloride dihydrate (1 mmol) in water (5 ml) was added. The resulting mixture was filtered, and the filtrate was set aside to crystallize at ambient temperature and in the presence of air providing, after three weeks, green crystals of (I) suitable for single-crystal X-ray diffraction.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms, with $\text{C}-\text{H}$ distances of 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene) and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for the methyl group, which was permitted to rotate but not to tilt, and $k = 1.2$ for all other H atoms. The reflection 200, which had been affected by the beam stop, was omitted from the data set.

Table 1
Experimental details.

Crystal data	
Chemical formula	[Cu(C ₉ H ₅ N ₄ O)Cl(C ₁₂ H ₈ N ₂)]
<i>M_r</i>	464.37
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	31.79 (3), 7.925 (6), 16.005 (13)
β (°)	97.69 (3)
<i>V</i> (Å ³)	3996 (6)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.25
Crystal size (mm)	0.27 × 0.23 × 0.14
Data collection	
Diffractometer	Bruker X8 APEXII area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.722, 0.804
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	34518, 4596, 3188
<i>R_{int}</i>	0.058
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.107, 1.05
No. of reflections	4596
No. of parameters	272
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.31, -0.37

Computer programs: *APEX2* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

In the final refinements, all reflections having $\theta > 27.5^\circ$ were omitted. Although the displacement parameters for atoms C121 and C122 are somewhat larger than those of the other atoms, no evidence was found for any positional disorder involving these two atoms.

3. Results and discussion

In the selected asymmetric unit of (I) (Fig. 1), the Cu^{II} centre is coordinated by a bidentate 1,10-phenanthroline unit, a

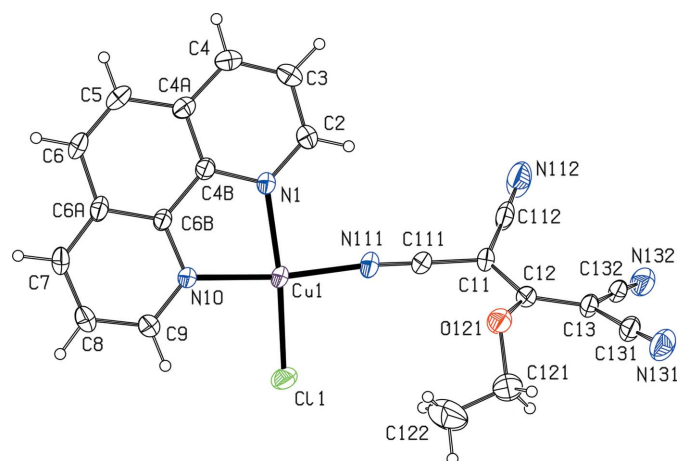


Figure 1
The selected asymmetric unit for compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

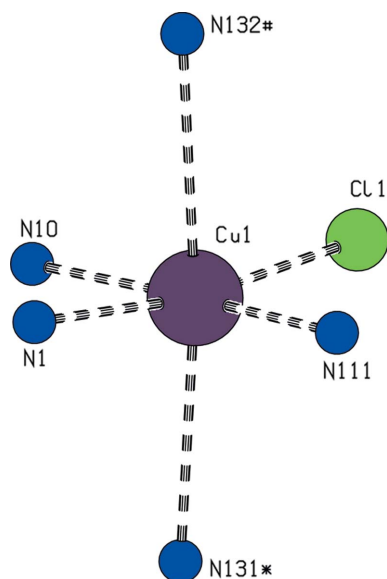


Figure 2
Part of the crystal structure of compound (I), showing the axially elongated (4 + 2) coordination at the Cu^{II} centre. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, -y, z + \frac{1}{2})$ and $(x, -y + 1, z + \frac{1}{2})$, respectively.

chloride ligand and a 1,1,3,3-tetracyano-2-ethoxypropenide ligand (hereafter denoted tcnobet) bonded *via* atom N111, where the two anionic ligands occupy mutually *cis* sites in a square-planar arrangement (Table 2). The usual axially elongated (4 + 2) coordination at the Cu^{II} atom is completed by N atoms from two further tcnobet ligands, namely atoms N131 and N132 at $(x, -y, z + \frac{1}{2})$ and $(x, -y + 1, z + \frac{1}{2})$, respectively (Fig. 2). Thus, the reference tcnobet ligand coordinates *via* atoms N111, N131 and N132 to the three Cu^{II} centres at $(x, y,$

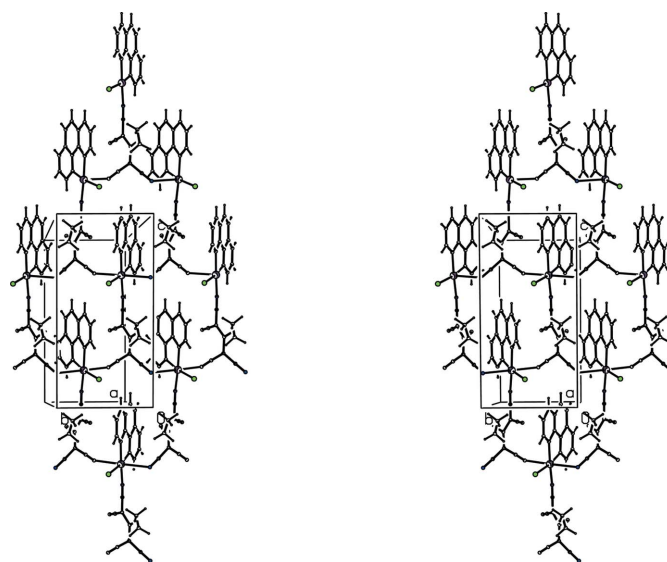


Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a two-dimensional coordination polymer lying parallel to (100) in the domain $0 < x < \frac{1}{4}$. For the sake of clarity, all H atoms have been omitted.

Table 2
Selected geometric parameters (Å, °).

Cu1—Cl1	2.2383 (16)	C5—C6	1.351 (4)
Cu1—N1	2.046 (2)	C6—C6A	1.436 (4)
Cu1—N10	2.019 (3)	C6A—C7	1.398 (4)
Cu1—N111	1.974 (3)	C7—C8	1.367 (4)
Cu1—N131 ⁱ	2.555 (3)	C8—C9	1.392 (4)
Cu1—N132 ⁱⁱ	2.758 (4)	C9—N10	1.328 (3)
N1—C2	1.328 (3)	N10—C6B	1.358 (3)
C2—C3	1.394 (4)	C6B—C4B	1.431 (4)
C3—C4	1.362 (4)	C4B—N1	1.360 (3)
C4—C4A	1.399 (4)	C4A—C4B	1.400 (4)
C4A—C5	1.434 (4)	C6A—C6B	1.399 (4)
Cl1—Cu1—N1	171.50 (6)	N131 ⁱ —Cu1—N10	90.17 (8)
Cl1—Cu1—N10	94.00 (7)	N131 ⁱ —Cu1—N111	90.05 (10)
Cl1—Cu1—N111	92.95 (8)	N132 ⁱⁱ —Cu1—Cl1	94.70 (7)
N1—Cu1—N10	81.27 (9)	N132 ⁱⁱ —Cu1—N1	78.69 (8)
N1—Cu1—N111	91.66 (10)	N132 ⁱⁱ —Cu1—N10	94.13 (8)
N10—Cu1—N111	172.91 (9)	N132 ⁱⁱ —Cu1—N111	83.98 (10)
N131 ⁱ —Cu1—Cl1	98.99 (8)	N131 ⁱ —Cu1—N132 ⁱⁱ	165.34 (10)
N131 ⁱ —Cu1—N1	88.14 (9)		
C111—C11—C12—C13	171.3 (2)	C11—C12—C13—C131	161.8 (3)
C112—C11—C12—C13	−13.6 (4)	C11—C12—C13—C132	−16.2 (4)

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

z), $(x, -y, z - \frac{1}{2})$ and $(x, -y + 1, z - \frac{1}{2})$, respectively. The coordination around the Cu^{II} centre is somewhat distorted from idealized geometry, with the angles between mutually *cis* pairs of ligating atoms ranging from 78.69 (8) to 98.99 (8)°, and those between *trans* pairs of ligands falling in the range 165.34 (10)–172.91 (9)° (Table 2 and Fig. 2)

The triply bridging coordination mode for the tcnobet ligand leads to the formation of a two-dimensional coordination polymer in the form of a sheet lying parallel to (100) in the domain $0 < x < \frac{1}{4}$ (Fig. 3). A second sheet of this type, related to the first by inversion lies in the domain $-\frac{1}{4} < x < 0$, while a second pair of sheets, related to the first by the *C*-centring operation, lie in the domains $\frac{1}{2} < x < \frac{3}{4}$ and $\frac{1}{4} < x < \frac{1}{2}$, respectively. There is a single direction-specific interaction between adjacent sheets in the form of a nearly linear C—H···N hydrogen bond (Table 3), whose effect is to link the two sheets in the domains $0 < x < \frac{1}{4}$ and $\frac{1}{4} < x < \frac{1}{2}$, which are related by the inversion centres at $x = \frac{1}{4}$, to form a bilayer; the chloride ligands lie on the outer surfaces of the bilayer, and the hydrogen bonds all lie in the central region (Fig. 4). Two bilayers, related to one another by the *C*-centring, pass through each unit cell. Hence, of the four N atoms in the tcnobet ligand, three are coordinated to different Cu^{II} centres as noted above and the fourth, atom N112, is involved in a hydrogen bond.

Within the 1,10-phenanthroline ligand, the bond lengths (Table 2) provide evidence for some bond fixation in the heterocyclic rings, while the C5—C6 bond in the carbocyclic ring is effectively an isolated double bond. Thus, in the heterocyclic rings, the N1—C2 and N10—C9 bonds are both significantly shorter than the N1—C4B and N10—C6B bonds, and the C3—C4 and C7—C8 bonds are the shortest C—C bonds in these rings. These observations all point to a mixture of forms **A** and **B** (see Scheme 1) as the dominant contributors to the electronic structure of this ligand.

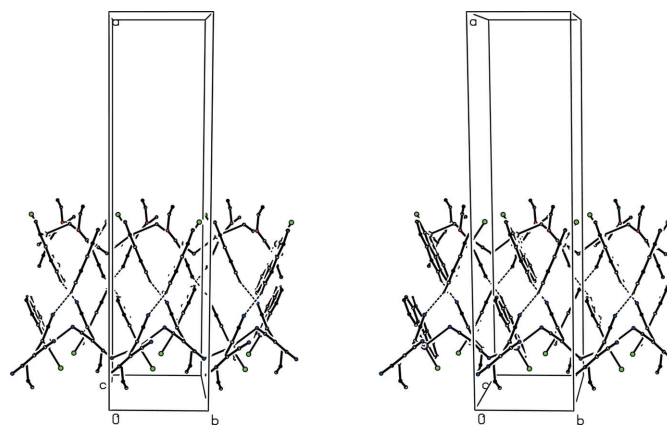
Table 3
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5···N112 ⁱⁱⁱ	0.93	2.55	3.450 (6)	163

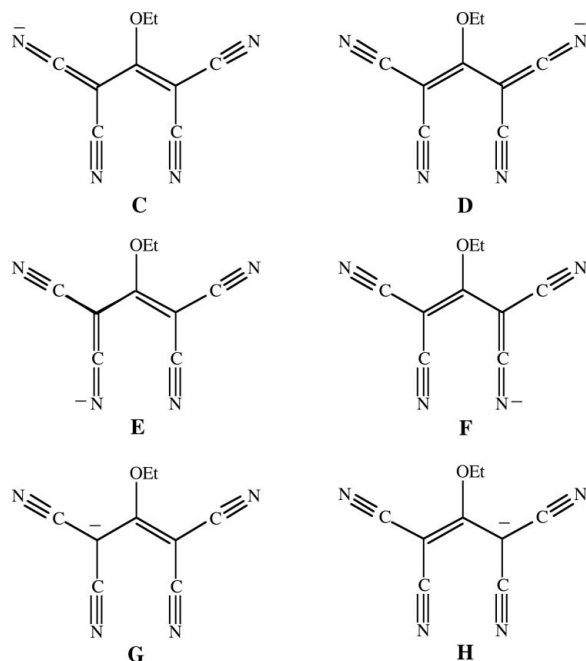
Symmetry code: (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

The bond lengths in the tcnobet ligand are very similar to those found in uncoordinated tcnobet anions in the hemihydrate salt [Fe(phen)₃](tcnobet)₂·0.5H₂O, (II) (Setifi *et al.*, 2013). In this salt, there are two independent anions, neither of which participates in any metal coordination; one of them acts as the acceptor in two independent O—H···N hydrogen bonds and the other is free from direction-specific intermolecular interactions. However, there are no significant differences between the corresponding bond lengths in the tcnobet ligand of (I) and the two tcnobet anions in (II), despite the differences in their crystal environments. In compound (I), the two central C—C bonds of the tcnobet ligand are similar in length; the C—C bond lengths to the nitrile substituents lie in the range 1.411 (4)–1.425 (4) Å and are all short for their type (Allen *et al.*, 1987), and the C—N bond lengths lie in the range 1.140 (4)–1.147 (4) Å, slightly short for their type.

Also significant is the similarity between the conformations of the tcnobet ligand in (I) (Table 2) and the uncoordinated anions in (II). In compound (I), the two $-C(CN)_2$ units are rotated out of the plane of the central C₃O unit in a conrotatory fashion. The dihedral angles between the central C₃O plane and the $-C(CN)_2$ planes containing atoms C11 and C13 are 14.2 (2) and 16.4 (2)°, respectively. Consideration of compound (I) in isolation might lead to the conclusion that the tcnobet conformation here is determined by the requirements of coordination to three independent Cu^{II} centres. However, in each of the two anions of compound (II), the rotation of the $-C(CN)_2$ units away from overall planarity is again conrotatory, and the corresponding dihedral angles are 16.9 (2) and 24.8 (2)° for the hydrogen-bonded anions, and 16.1 (2) and 18.9 (2)° for the free anion. In an Fe^{II} salt, denoted (III),

**Figure 4**
A stereoview of part of the crystal structure of compound (I), showing the pairwise linking of coordination polymer sheets by hydrogen bonds. For the sake of clarity, H atoms other than H5 have been omitted.

containing the related anion 1,1,3,3-tetracyano-2-(methylsulfanyl)propenide (tcnsme; Setifi *et al.*, 2010), the two independent anions both show conrotatory displacements of the $-\text{C}(\text{CN})_2$ units away from the central C_3S planes, with dihedral angles ranging from 12.3 (4) to 24.4 (4) $^\circ$, rather similar to the range of values in tcnouet units, noted above. The similarity of the tcnouet and tcnsme conformations in compounds (I)–(III), regardless of the number and nature of their participation in direction-specific intermolecular interactions, suggests that these conformations may be an intrinsic property of these species.



Scheme 2

Accordingly, the electronic structure of the tcnouet ligand in (I) is of interest. The close similarity of the C–N distances, and within the two types of C–C distance, indicates a highly symmetric electronic structure with the negative charge distributed over the four N atoms, forms **C–F** (see Scheme 2), as well as over the two terminal C atoms of the allylic portion,

forms **G** and **H**. A modest deviation from planarity, as observed here, provides no significant impediment to the delocalization of electronic charge (*cf.* Cobo *et al.*, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3522). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2014). **C70**, 19–22 [doi:10.1107/S2053229613032804]

Poly[[chlorido(1,10-phenanthroline- κ^2N,N')copper(II)]- μ_3 -1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa^3N:N':N''$]: coordination polymer sheets linked into bilayers by hydrogen bonds

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Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Poly[[chlorido(1,10-phenanthroline- κ^2N,N')copper(II)]- μ_3 -1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa^3N:N':N''$]

Crystal data

[Cu(C₉H₅N₄O)Cl(C₁₂H₈N₂)]

$M_r = 464.37$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 31.79$ (3) Å

$b = 7.925$ (6) Å

$c = 16.005$ (13) Å

$\beta = 97.69$ (3)°

$V = 3996$ (6) Å³

$Z = 8$

$F(000) = 1880$

$D_x = 1.544$ Mg m⁻³

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

Cell parameters from 6366 reflections

$\theta = 2.6$ – 31.0 °

$\mu = 1.25$ mm⁻¹

$T = 296$ K

Plate, green

$0.27 \times 0.23 \times 0.14$ mm

Data collection

Bruker X8 APEXII area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.722$, $T_{\max} = 0.804$

34518 measured reflections

4596 independent reflections

3188 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.6$ °

$h = -41 \rightarrow 41$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.107$

$S = 1.05$

4596 reflections

272 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.7334P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{Å}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu1	0.109132 (10)	0.30029 (4)	0.695410 (18)	0.03960 (12)
Cl1	0.05105 (2)	0.44903 (10)	0.64741 (5)	0.0578 (2)
N1	0.16459 (7)	0.1941 (2)	0.75086 (13)	0.0384 (5)
C2	0.19716 (9)	0.1342 (4)	0.71602 (18)	0.0504 (7)
H2	0.1960	0.1372	0.6577	0.061*
C3	0.23308 (9)	0.0670 (4)	0.7640 (2)	0.0601 (8)
H3	0.2552	0.0249	0.7374	0.072*
C4	0.23586 (9)	0.0630 (4)	0.8496 (2)	0.0586 (8)
H4	0.2600	0.0195	0.8818	0.070*
C4A	0.20220 (8)	0.1247 (3)	0.88875 (17)	0.0442 (6)
C4B	0.16713 (8)	0.1896 (3)	0.83635 (15)	0.0365 (5)
C5	0.20146 (10)	0.1260 (4)	0.97815 (18)	0.0565 (8)
H5	0.2248	0.0849	1.0136	0.068*
C6	0.16767 (10)	0.1857 (3)	1.01196 (17)	0.0526 (7)
H6	0.1681	0.1853	1.0702	0.063*
C6A	0.13105 (9)	0.2496 (3)	0.95917 (15)	0.0428 (6)
C6B	0.13112 (8)	0.2516 (3)	0.87180 (15)	0.0355 (5)
C7	0.09436 (10)	0.3073 (3)	0.98932 (17)	0.0507 (7)
H7	0.0929	0.3090	1.0470	0.061*
C8	0.06066 (10)	0.3611 (4)	0.93366 (19)	0.0558 (7)
H8	0.0359	0.3976	0.9531	0.067*
C9	0.06358 (9)	0.3610 (3)	0.84764 (18)	0.0483 (7)
H9	0.0405	0.3988	0.8105	0.058*
N10	0.09806 (6)	0.3090 (2)	0.81664 (13)	0.0370 (5)
C11	0.14488 (9)	0.2787 (3)	0.43121 (16)	0.0421 (6)
C12	0.11597 (8)	0.2046 (3)	0.36808 (16)	0.0411 (6)
C13	0.11784 (9)	0.2112 (3)	0.28176 (15)	0.0423 (6)
C111	0.13474 (9)	0.2791 (3)	0.51440 (17)	0.0448 (6)
N111	0.12696 (8)	0.2807 (3)	0.58229 (15)	0.0523 (6)
C112	0.18515 (11)	0.3424 (4)	0.41863 (17)	0.0564 (8)
N112	0.21808 (10)	0.3930 (5)	0.41061 (18)	0.0888 (10)
O121	0.08607 (6)	0.1140 (3)	0.39883 (12)	0.0552 (5)
C121	0.04102 (10)	0.1324 (5)	0.3638 (2)	0.0801 (11)
H21A	0.0377	0.2240	0.3233	0.096*
H21B	0.0309	0.0294	0.3352	0.096*
C122	0.01714 (14)	0.1667 (7)	0.4313 (4)	0.130 (2)
H22A	-0.0118	0.1891	0.4088	0.196*
H22B	0.0289	0.2634	0.4622	0.196*
H22C	0.0183	0.0709	0.4682	0.196*
C131	0.09473 (10)	0.0948 (3)	0.22534 (17)	0.0503 (7)
N131	0.07748 (10)	-0.0037 (3)	0.18067 (17)	0.0710 (8)

C132	0.14346 (9)	0.3290 (3)	0.24406 (17)	0.0450 (6)
N132	0.16247 (9)	0.4237 (3)	0.21067 (16)	0.0617 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0404 (2)	0.0556 (2)	0.02246 (18)	0.00481 (14)	0.00309 (13)	0.00303 (12)
Cl1	0.0434 (4)	0.0846 (5)	0.0444 (4)	0.0096 (3)	0.0016 (3)	0.0217 (3)
N1	0.0375 (12)	0.0507 (11)	0.0273 (11)	0.0018 (9)	0.0053 (9)	-0.0002 (9)
C2	0.0427 (16)	0.0718 (17)	0.0386 (16)	0.0057 (13)	0.0122 (13)	-0.0008 (13)
C3	0.0394 (16)	0.084 (2)	0.059 (2)	0.0145 (14)	0.0147 (15)	-0.0004 (16)
C4	0.0384 (16)	0.080 (2)	0.055 (2)	0.0130 (14)	-0.0019 (14)	0.0055 (15)
C4A	0.0388 (15)	0.0538 (14)	0.0378 (15)	0.0010 (11)	-0.0030 (12)	0.0010 (11)
C4B	0.0371 (14)	0.0428 (12)	0.0293 (14)	-0.0028 (10)	0.0032 (11)	0.0001 (9)
C5	0.0547 (19)	0.0720 (18)	0.0375 (17)	0.0061 (15)	-0.0133 (14)	0.0058 (13)
C6	0.062 (2)	0.0689 (17)	0.0241 (14)	0.0041 (14)	-0.0038 (13)	0.0008 (12)
C6A	0.0544 (17)	0.0492 (13)	0.0243 (13)	0.0007 (12)	0.0034 (12)	-0.0006 (10)
C6B	0.0371 (14)	0.0436 (12)	0.0251 (13)	-0.0007 (10)	0.0023 (11)	0.0003 (9)
C7	0.0625 (19)	0.0647 (16)	0.0267 (14)	0.0034 (14)	0.0128 (13)	-0.0029 (12)
C8	0.0533 (18)	0.0749 (18)	0.0432 (18)	0.0107 (15)	0.0216 (15)	-0.0007 (14)
C9	0.0416 (16)	0.0652 (16)	0.0393 (16)	0.0104 (13)	0.0097 (13)	0.0023 (12)
N10	0.0341 (11)	0.0495 (11)	0.0275 (11)	0.0042 (9)	0.0045 (9)	0.0012 (8)
C11	0.0451 (15)	0.0578 (15)	0.0235 (13)	0.0059 (12)	0.0053 (11)	-0.0010 (10)
C12	0.0412 (15)	0.0497 (14)	0.0321 (14)	0.0105 (11)	0.0036 (12)	0.0009 (10)
C13	0.0506 (16)	0.0495 (14)	0.0255 (14)	0.0084 (12)	0.0003 (12)	-0.0033 (10)
C111	0.0448 (16)	0.0580 (15)	0.0301 (15)	0.0084 (12)	-0.0005 (12)	-0.0010 (11)
N111	0.0539 (15)	0.0763 (16)	0.0267 (13)	0.0026 (12)	0.0051 (11)	-0.0015 (11)
C112	0.061 (2)	0.083 (2)	0.0246 (15)	-0.0050 (16)	0.0019 (14)	-0.0071 (13)
N112	0.068 (2)	0.153 (3)	0.0455 (18)	-0.040 (2)	0.0069 (15)	-0.0122 (18)
O121	0.0469 (12)	0.0730 (12)	0.0453 (12)	-0.0016 (10)	0.0050 (9)	0.0058 (9)
C121	0.046 (2)	0.121 (3)	0.071 (3)	-0.0071 (19)	-0.0003 (18)	-0.016 (2)
C122	0.062 (3)	0.190 (5)	0.142 (5)	0.014 (3)	0.024 (3)	-0.022 (4)
C131	0.0620 (19)	0.0557 (15)	0.0317 (15)	0.0120 (13)	0.0003 (14)	0.0000 (12)
N131	0.089 (2)	0.0700 (17)	0.0493 (17)	0.0026 (15)	-0.0084 (15)	-0.0145 (13)
C132	0.0503 (17)	0.0567 (15)	0.0261 (14)	0.0137 (13)	-0.0022 (12)	-0.0038 (11)
N132	0.0654 (17)	0.0765 (17)	0.0425 (15)	0.0009 (14)	0.0045 (13)	0.0103 (13)

Geometric parameters (Å, °)

Cu1—Cl1	2.2383 (16)	C9—H9	0.9300
Cu1—N1	2.046 (2)	N10—C6B	1.358 (3)
Cu1—N10	2.019 (3)	C6B—C4B	1.431 (4)
Cu1—N111	1.974 (3)	C4B—N1	1.360 (3)
Cu1—N131 ⁱ	2.555 (3)	C4A—C4B	1.400 (4)
Cu1—N132 ⁱⁱ	2.758 (4)	C6A—C6B	1.399 (4)
N1—C2	1.328 (3)	C11—C12	1.401 (4)
C2—C3	1.394 (4)	C11—C111	1.411 (4)
C2—H2	0.9300	C11—C112	1.416 (4)
C3—C4	1.362 (4)	C12—O121	1.337 (3)
C3—H3	0.9300	C12—C13	1.392 (4)

C4—C4A	1.399 (4)	C13—C131	1.424 (4)
C4—H4	0.9300	C13—C132	1.425 (4)
C4A—C5	1.434 (4)	C111—N111	1.146 (4)
C5—C6	1.351 (4)	C112—N112	1.144 (4)
C5—H5	0.9300	O121—C121	1.474 (4)
C6—C6A	1.436 (4)	C121—C122	1.426 (5)
C6—H6	0.9300	C121—H21A	0.9700
C6A—C7	1.398 (4)	C121—H21B	0.9700
C7—C8	1.367 (4)	C122—H22A	0.9600
C7—H7	0.9300	C122—H22B	0.9600
C8—C9	1.392 (4)	C122—H22C	0.9600
C8—H8	0.9300	C131—N131	1.147 (4)
C9—N10	1.328 (3)	C132—N132	1.140 (4)
Cl1—Cu1—N1	171.50 (6)	N10—C6B—C6A	123.3 (2)
Cl1—Cu1—N10	94.00 (7)	N10—C6B—C4B	116.6 (2)
Cl1—Cu1—N111	92.95 (8)	C6A—C6B—C4B	120.1 (2)
N1—Cu1—N10	81.27 (9)	C8—C7—C6A	119.7 (3)
N1—Cu1—N111	91.66 (10)	C8—C7—H7	120.2
N10—Cu1—N111	172.91 (9)	C6A—C7—H7	120.2
N131 ⁱ —Cu1—Cl1	98.99 (8)	C7—C8—C9	119.6 (3)
N131 ⁱ —Cu1—N1	88.14 (9)	C7—C8—H8	120.2
N131 ⁱ —Cu1—N10	90.17 (8)	C9—C8—H8	120.2
N131 ⁱ —Cu1—N111	90.05 (10)	N10—C9—C8	122.5 (3)
N132 ⁱⁱ —Cu1—Cl1	94.70 (7)	N10—C9—H9	118.7
N132 ⁱⁱ —Cu1—N1	78.69 (8)	C8—C9—H9	118.7
N132 ⁱⁱ —Cu1—N10	94.13 (8)	C9—N10—C6B	117.8 (2)
N132 ⁱⁱ —Cu1—N111	83.98 (10)	C9—N10—Cu1	128.95 (18)
N131 ⁱ —Cu1—N132 ⁱⁱ	165.34 (10)	C6B—N10—Cu1	113.20 (17)
C2—N1—C4B	117.9 (2)	C12—C11—C111	118.1 (3)
C2—N1—Cu1	129.80 (19)	C12—C11—C112	124.5 (2)
C4B—N1—Cu1	112.27 (16)	C111—C11—C112	117.3 (2)
N1—C2—C3	122.2 (3)	O121—C12—C13	120.8 (2)
N1—C2—H2	118.9	O121—C12—C11	113.0 (2)
C3—C2—H2	118.9	C13—C12—C11	126.1 (3)
C4—C3—C2	120.1 (3)	C12—C13—C131	121.2 (3)
C4—C3—H3	120.0	C12—C13—C132	123.2 (2)
C2—C3—H3	120.0	C131—C13—C132	115.6 (2)
C3—C4—C4A	119.5 (3)	N111—C111—C11	179.1 (3)
C3—C4—H4	120.3	C111—N111—Cu1	174.3 (2)
C4A—C4—H4	120.3	N112—C112—C11	178.2 (3)
C4—C4A—C4B	117.1 (3)	C12—O121—C121	120.7 (2)
C4—C4A—C5	124.4 (3)	C122—C121—O121	108.7 (3)
C4B—C4A—C5	118.5 (2)	C122—C121—H21A	110.0
N1—C4B—C4A	123.2 (2)	O121—C121—H21A	110.0
N1—C4B—C6B	116.5 (2)	C122—C121—H21B	110.0
C4A—C4B—C6B	120.3 (2)	O121—C121—H21B	110.0
C6—C5—C4A	121.5 (3)	H21A—C121—H21B	108.3
C6—C5—H5	119.3	C121—C122—H22A	109.5

C4A—C5—H5	119.3	C121—C122—H22B	109.5
C5—C6—C6A	120.9 (3)	H22A—C122—H22B	109.5
C5—C6—H6	119.6	C121—C122—H22C	109.5
C6A—C6—H6	119.6	H22A—C122—H22C	109.5
C7—C6A—C6B	117.0 (2)	H22B—C122—H22C	109.5
C7—C6A—C6	124.1 (3)	N131—C131—C13	177.1 (3)
C6B—C6A—C6	118.8 (3)	N132—C132—C13	176.7 (3)
N111—Cu1—N1—C2	-2.0 (2)	C4A—C4B—C6B—N10	-178.6 (2)
N10—Cu1—N1—C2	178.4 (2)	N1—C4B—C6B—C6A	179.3 (2)
N111—Cu1—N1—C4B	176.87 (17)	C4A—C4B—C6B—C6A	0.8 (4)
N10—Cu1—N1—C4B	-2.66 (16)	C6B—C6A—C7—C8	0.4 (4)
C4B—N1—C2—C3	0.4 (4)	C6—C6A—C7—C8	-178.0 (3)
Cu1—N1—C2—C3	179.3 (2)	C6A—C7—C8—C9	-1.2 (4)
N1—C2—C3—C4	-0.8 (5)	C7—C8—C9—N10	0.5 (5)
C2—C3—C4—C4A	0.8 (5)	C8—C9—N10—C6B	1.1 (4)
C3—C4—C4A—C4B	-0.6 (4)	C8—C9—N10—Cu1	-179.4 (2)
C3—C4—C4A—C5	179.6 (3)	C6A—C6B—N10—C9	-2.1 (4)
C2—N1—C4B—C4A	-0.2 (4)	C4B—C6B—N10—C9	177.4 (2)
Cu1—N1—C4B—C4A	-179.24 (19)	C6A—C6B—N10—Cu1	178.4 (2)
C2—N1—C4B—C6B	-178.6 (2)	C4B—C6B—N10—Cu1	-2.2 (3)
Cu1—N1—C4B—C6B	2.3 (3)	N1—Cu1—N10—C9	-176.9 (2)
C4—C4A—C4B—N1	0.2 (4)	Cl1—Cu1—N10—C9	10.2 (2)
C5—C4A—C4B—N1	-179.9 (2)	N1—Cu1—N10—C6B	2.62 (16)
C4—C4A—C4B—C6B	178.6 (2)	Cl1—Cu1—N10—C6B	-170.27 (16)
C5—C4A—C4B—C6B	-1.5 (4)	C111—C11—C12—O121	-12.4 (3)
C4—C4A—C5—C6	-179.2 (3)	C112—C11—C12—O121	162.7 (3)
C4B—C4A—C5—C6	1.0 (4)	C111—C11—C12—C13	171.3 (2)
C4A—C5—C6—C6A	0.2 (4)	C112—C11—C12—C13	-13.6 (4)
C5—C6—C6A—C7	177.5 (3)	O121—C12—C13—C131	-14.2 (4)
C5—C6—C6A—C6B	-0.9 (4)	C11—C12—C13—C131	161.8 (3)
C7—C6A—C6B—N10	1.3 (4)	O121—C12—C13—C132	167.7 (2)
C6—C6A—C6B—N10	179.8 (2)	C11—C12—C13—C132	-16.2 (4)
C7—C6A—C6B—C4B	-178.1 (2)	C13—C12—O121—C121	-50.1 (4)
C6—C6A—C6B—C4B	0.4 (4)	C11—C12—O121—C121	133.4 (3)
N1—C4B—C6B—N10	-0.1 (3)	C12—O121—C121—C122	-126.9 (4)

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 ⁱⁱⁱ —N112 ⁱⁱⁱ	0.93	2.55	3.450 (6)	163

Symmetry code: (iii) $-x+1/2, y-1/2, -z+3/2$.