

# Crystal structure and Hirshfeld surface of a pentaamminecopper(II) complex with urea and chloride

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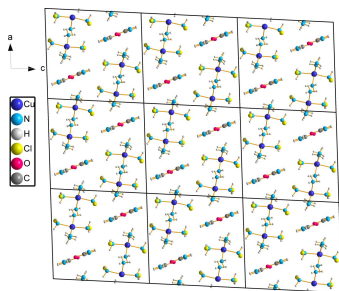
**Supporting information:** this article has supporting information at journals.iucr.org/e

The reaction of copper(II) oxalate and hexamethylenetetramine in a deep eutectic solvent made of urea and choline chloride produced crystals of pentaamminecopper(II) dichloride–urea (1/1),  $[\text{Cu}(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{CO}(\text{NH}_2)_2$ , which was characterized by single-crystal X-ray diffraction. The complex contains discrete pentaamminecopper(II) units in a square-based pyramidal geometry. The overall structure of the multi-component crystal is dictated by hydrogen bonding between urea molecules and amine H atoms with chloride anions.

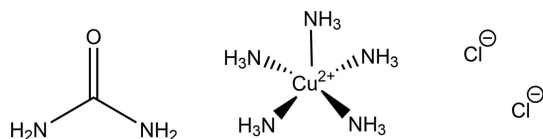
## 1. Chemical context

Copper oxalate,  $\text{Cu}(\text{ox})$ , is primarily a synthetic compound that has been the subject of much research and can also be found naturally as the mineral moolooite (Clarke & Williams, 1986). It has been examined as a potential precursor to forming copper oxide particles with controlled morphologies (Rahimi-Nasrabadi *et al.*, 2013) and has been the subject of thorough investigation of its structure (Fichtner-Schmittler, 1984; O'Connor *et al.*, 2019; Korniyakov *et al.*, 2023). Unlike other first row transition-metal oxalate compounds, which form mainly as dihydrates, copper oxalate forms as anhydrous chains with chemisorbed water on the particle's surface, with the amount of water being dependent on the reaction conditions. The amount of water present also contributes to disorder (O'Connor *et al.*, 2019; Korniyakov *et al.*, 2023). Copper oxalate forms as a microcrystalline powder so we were interested in investigating the use of alternative solvents that could allow for the synthesis of single crystals of anhydrous copper oxalate compounds.

Ionic liquids have been used to tune reaction conditions such as solubility and have also been utilized in the synthesis of coordination compounds to help with templating of the structure (Dybtsev *et al.*, 2004). However, cost can be a prohibitive factor in their use and so deep eutectic solvents, mixtures that have melting points drastically lower than the individual components, can be a cheaper alternative (Zhang *et al.*, 2009). Choline chloride and urea are commonly used as a deep eutectic solvent due to the melting point of 285 K for the eutectic mixture, which is considerably lower than the components' own, with melting points of 575 and 406 K, respectively (Abbott *et al.*, 2003). In the presence of hexamethylenetetramine the solvent allows copper oxalate to be dissolved when heated. With this in mind, the investigation of copper compounds that could form from deep eutectic solvents was carried out with the intent of forming crystalline anhydrous copper oxalate compounds. In this particular case,



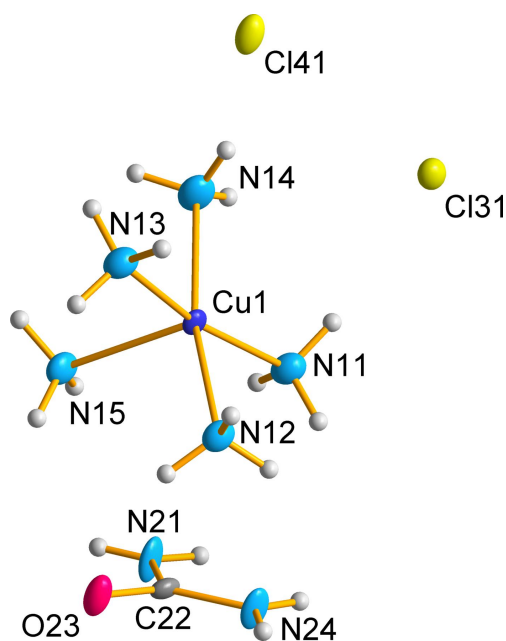
while this did not occur, we have obtained a copper(II) complex with ammonia ligands, urea and chloride,  $[\text{Cu}(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{CO}(\text{NH}_2)_2$ .



The formation of this copper(II) complex is thought to occur through the decomposition of urea to release ammonia, which is the source of the ligands. Pentaaminecopper(II) complexes are known to form when excess ammonia is present (Cotton & Wilkinson, 1972). Ammonia out-competes choline, chloride and urea as a ligand for copper(II), resulting in the pentaaminecopper(II) complex. Despite this, pentaaminecopper(II) complexes rarely crystallize, likely due to the volatility of the ammonia ligand.

## 2. Structural commentary

This multi-component crystal (MCC) crystallizes in the  $P2_1/n$  setting of the space group  $P2_1/c$  (no. 14). The asymmetric unit (ASU) contains one copper(II) ion coordinated by five ammonia ligands, one urea molecule and two chloride anions (Fig. 1). The copper ion shows a slightly distorted square-based pyramidal geometry, with four of the ammonia ligands lying on a distorted square plane ( $N_{\text{eq}}$ ) and one ammonia forming the vertex ( $N_{\text{ax}}$ ). The equatorial  $\text{Cu}-N_{\text{eq}}$  (N11–N14) bond lengths range from 2.0313 (19) to 2.050 (2) Å with an average of 2.039 Å. The axial  $\text{Cu}-N15$  bond is longer than the equatorial  $\text{Cu}-N_{\text{eq}}$  (N11–N14) bonds due to anti-bonding



**Figure 1**  
Asymmetric unit of the pentaaminecopper complex showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 75% probability level.

**Table 1**  
Selected geometric parameters (Å, °).

|             |             |             |             |
|-------------|-------------|-------------|-------------|
| Cu1–N11     | 2.039 (2)   | Cu1–N14     | 2.0339 (19) |
| Cu1–N12     | 2.0313 (19) | Cu1–N15     | 2.2107 (19) |
| Cu1–N13     | 2.050 (2)   |             |             |
| N11–Cu1–N15 | 98.65 (7)   | N13–Cu1–N15 | 91.61 (7)   |
| N12–Cu1–N15 | 99.60 (8)   | N14–Cu1–N15 | 94.55 (8)   |

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

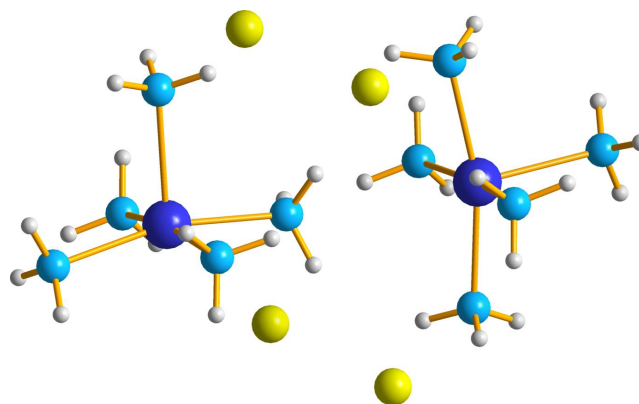
| <i>D</i> –H··· <i>A</i>        | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|--------------------------------|-------------|---------------|-----------------------|-------------------------|
| N11–H11A···Cl41 <sup>i</sup>   | 0.91        | 2.79          | 3.509 (2)             | 137                     |
| N11–H11B···Cl31                | 0.91        | 2.54          | 3.443 (2)             | 170                     |
| N11–H11C···Cl41 <sup>ii</sup>  | 0.91        | 2.82          | 3.541 (2)             | 137                     |
| N12–H12A···Cl31 <sup>i</sup>   | 0.91        | 2.57          | 3.461 (2)             | 167                     |
| N12–H12B···Cl41 <sup>i</sup>   | 0.91        | 2.67          | 3.4273 (19)           | 142                     |
| N13–H13A···Cl31 <sup>iii</sup> | 0.91        | 2.49          | 3.381 (2)             | 166                     |
| N13–H13C···Cl31 <sup>i</sup>   | 0.91        | 2.69          | 3.4752 (15)           | 145                     |
| N14–H14A···Cl31 <sup>ii</sup>  | 0.91        | 2.56          | 3.430 (2)             | 160                     |
| N14–H14C···Cl41                | 0.91        | 2.55          | 3.418 (2)             | 159                     |
| N15–H15A···Cl31 <sup>ii</sup>  | 0.91        | 2.68          | 3.530 (2)             | 157                     |
| N21–H21A···O23 <sup>iv</sup>   | 0.79 (3)    | 2.11 (3)      | 2.893 (3)             | 172 (3)                 |
| N21–H21B···Cl41 <sup>v</sup>   | 0.87 (3)    | 2.50 (3)      | 3.315 (2)             | 158 (2)                 |
| N24–H24A···O23 <sup>vi</sup>   | 0.81 (3)    | 2.10 (3)      | 2.906 (3)             | 173 (3)                 |
| N24–H24B···Cl41 <sup>v</sup>   | 0.88 (3)    | 2.50 (3)      | 3.319 (2)             | 157 (3)                 |

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

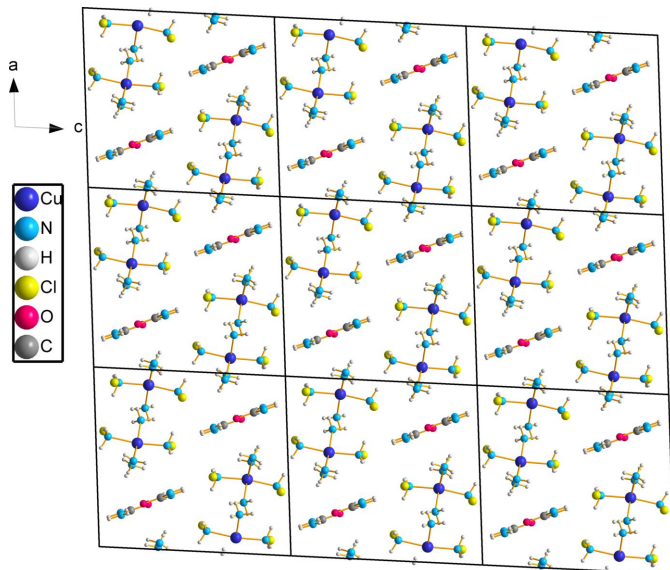
electron density down the axial axis (Halcrow, 2013), with a bond length of 2.2107 (19) Å (Table 1). The bond angles between the  $N_{\text{eq}}-\text{Cu}-N_{\text{ax}}$  are slightly above 90° and range from 91.61 (7) to 99.60 (8)° (Table 1). There are no atoms within the van der Waals radius of the copper at the basal site with the nearest species being the hydrogen atoms on another pentaaminecopper(II) complex (Fig. 2). This nearest hydrogen atom is located 3.091 Å away, confirming the square-based pyramidal geometry of the complex.

## 3. Supramolecular features

Each pentaaminecopper(II) complex forms  $\text{N}-\text{H}\cdots\text{Cl}$  contacts to neighbouring chloride ions. Cl31 forms contacts to



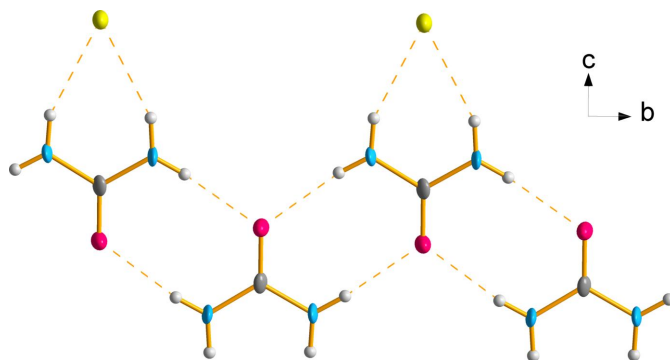
**Figure 2**  
Geometry of the pentaaminecopper(II) complex, with view of the basal site shown confirming the square-based pyramidal geometry



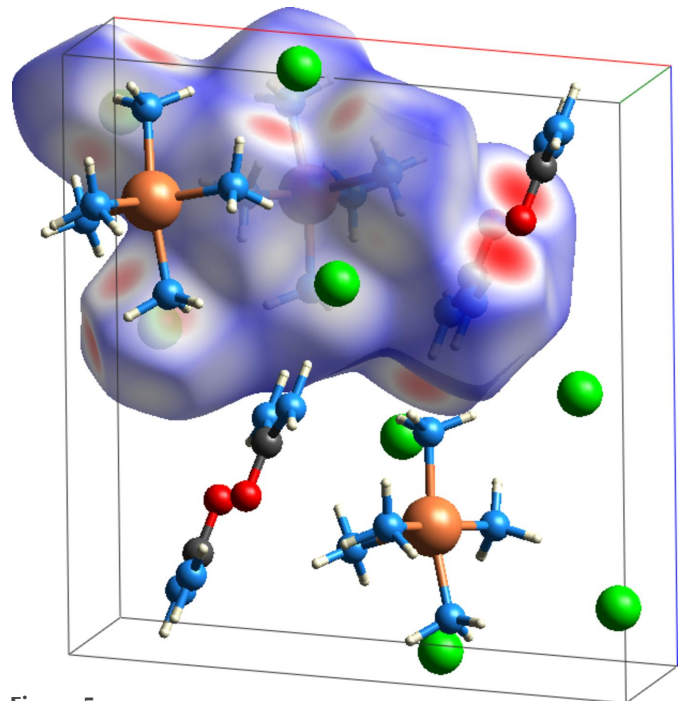
**Figure 3**  
Crystal packing viewed down the  $b$  axis.

four different pentaaminecopper(II) complexes and Cl41 forms contacts to three different pentaaminecopper(II) complexes to create a repeating array of copper ions down the  $b$  axis (Fig. 3). These hydrogen bonds have an average  $N\cdots Cl$  distance of 3.453 Å and range from 3.381 (2) to 3.541 (2) Å (Table 2). The urea molecules also form  $N-H\cdots Cl41$  contacts with an average  $N\cdots Cl41$  distance of 3.317 Å (Table 2). The hydrogens on the urea molecule which do not hydrogen bond with chloride ions instead form hydrogen bonds with other urea molecules with an average  $N\cdots O$  distance of 2.900 Å (Table 2). The urea molecules form a ribbon down the  $b$  axis between copper ions with every other urea molecule facing an alternate direction along the  $c$  axis (Fig. 4).

The Hirshfeld surface analysis (Fig. 5) and two-dimensional fingerprint plots (Fig. 6) were calculated using *Crystal Explorer 17* (Spackman *et al.*, 2021). The colours of the surface relate to the distance of the contacts with red surfaces indicating contacts shorter than the van der Waals radii, white surfaces indicating contacts near the van der Waals radii and

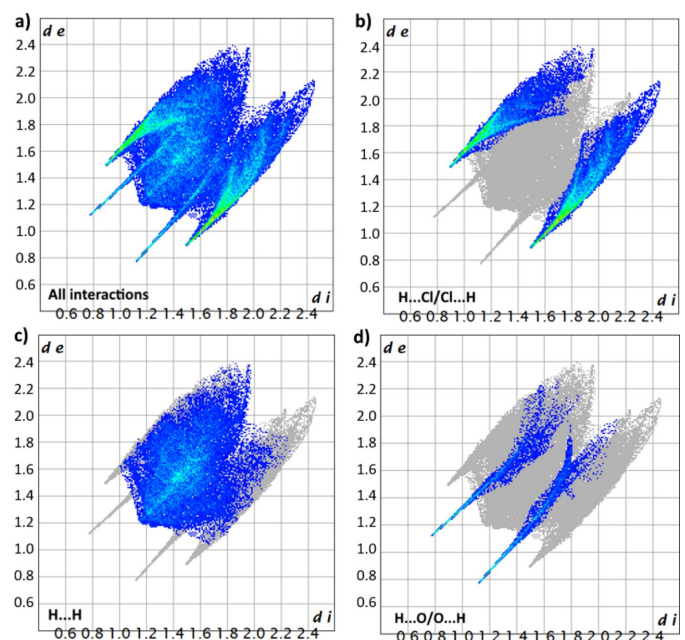


**Figure 4**  
Hydrogen bonding (indicated by the orange dashed lines) between urea molecules and chloride ions viewed down the  $a$  axis. Displacement ellipsoids are drawn at the 75% probability level.



**Figure 5**  
Hirshfeld surface of pentaamine copper complex mapped over  $d_{\text{norm}}$

blue surfaces indicating contacts longer than the van der Waals radii.  $N-H\cdots O$  hydrogen bonds between urea molecules,  $N-H\cdots Cl$  hydrogen bonds between chloride and ammonia, and  $N-H\cdots Cl$  hydrogen bonds between chloride and urea are indicated by red surfaces.  $H\cdots H$  contacts (43.1%) and  $H\cdots Cl/Cl\cdots H$  contacts (42.2%) make up the bulk of the contribution to the Hirshfeld surface while  $H\cdots O/O\cdots H$  contacts contribute 9.9%.



**Figure 6**  
Two-dimensional fingerprint plots showing: (a) all interactions, (b)  $H\cdots Cl/Cl\cdots H$  contacts, (c)  $H\cdots H$  contacts and (d)  $H\cdots O/O\cdots H$  contacts.

#### 4. Database survey

There are few pentaamminecopper(II) complexes present in the Cambridge Structural Database (CSD version 5.43, November 2021 update; Groom *et al.*, 2016) with five reported in total, of which only three displayed square-based pyramidal geometry (refcode: BAWLES, Mironov *et al.*, 2012; refcode: BAWLOC, Mironov *et al.*, 2012 and refcode: ONEVIN, Mironov *et al.*, 2011). Interestingly, in one of these entries the MCC contains pentaamminecopper(II) complexes in both square-based pyramidal and trigonal-bipyramidal geometry (refcode: BAWLES, Mironov *et al.*, 2012). These complexes are unusual given that axial bond elongation should result in the axial ligands being more labile. Coupled with ammonia being a volatile ligand this likely gives rise to the rarity of these complexes in the solid state. Due to the paucity of these complexes in the literature, similar complexes were examined where at least three ammonia ligands were present and where one of those was present in the axial position. This only resulted in one additional complex being found, a triamine(ethylenediamine)-copper(II) complex (refcode: GAFYET, Mironov *et al.*, 2008). In each of these examples, the copper complex was the cationic counterpart to an anionic cluster. Additionally, in the copper complexes the axial N–Cu bond was always longer than the equatorial N–Cu bond, which is consistent with what has been found in our complex. The literature equatorial N–Cu bonds ranged in value from 1.98 to 2.06 Å with an average of 2.04 Å, while the axial N–Cu bonds were longer and ranged in value from 2.24 to 2.33 Å with an average of 2.28 Å.

#### 5. Synthesis and crystallization

Choline chloride (1.3963 g, 10.0 mmol) and urea (1.2058 g, 20.0 mmol) were mixed and heated to 333 K until a homogenous liquid formed. Copper(II) oxalate (0.1682 g, 1.0 mmol) was added to the liquid with stirring to form a suspension. The mixture was poured into a Teflon-lined autoclave and hexamethylenetetramine (0.0690 g, 0.5 mmol) was added. The autoclave was closed and placed in an oven at 393 K for 48 h before cooling to room temperature over 12 h. The resulting blue liquid was poured into a vial and was capped and was left undisturbed for several months to produce dark-blue needles up to 3 mm in length. Due to the large size of these crystals they were cut to a block shape to be mounted on the diffractometer. Attempts to isolate the crystals were unsuccessful due to the solvent being too viscous to filter and attempts to dilute this with water or alcohol resulted in dissolution of the crystals. A yield of 10 mg was estimated from the crystal size and density.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarised in Table 3. Urea hydrogen atoms were located in a difference-Fourier map and refined freely. Ammonia hydrogens could be located in a difference-Fourier map but

**Table 3**  
Experimental details.

|   |   |
|---|---|
| Crystal data  |   |
| Chemical formula  | [Cu(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>2</sub> ·CH <sub>4</sub> N <sub>2</sub> O |
| <i>M<sub>r</sub></i>  | 279.67  |
| Crystal system, space group   | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>  |
| Temperature (K)   | 100   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)  | 12.2214 (2), 7.0230 (1), 13.0537 (3)  |
| $\beta$ (°)   | 94.511 (2)  |
| <i>V</i> (Å <sup>3</sup> )  | 1116.94 (4)   |
| <i>Z</i>  | 4   |
| Radiation type  | Cu <i>K</i> $\alpha$  |
| $\mu$ (mm <sup>-1</sup> )   | 7.01  |
| Crystal size (mm)   | 0.45 × 0.22 × 0.12  |
| Data collection   |   |
| Diffractometer  | SuperNova, Dual, Cu at home/<br>near, Atlas   |
| Absorption correction   | Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku<br>OD, 2021)                                |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>   | 0.229, 1.000  |
| No. of measured, independent and<br>observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections                          | 12732, 1977, 1835   |
| <i>R</i> <sub>int</sub><br>( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )                                  | 0.059<br>0.595  |
| Refinement  |   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.033, 0.092, 1.08  |
| No. of reflections  | 1977  |
| No. of parameters   | 130   |
| H-atom treatment  | H atoms treated by a mixture of<br>independent and constrained<br>refinement          |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )  | 0.67, -0.80   |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

free refinement of them was unstable so they were positioned geometrically and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  for NH<sub>3</sub> hydrogen atoms.

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## supporting information

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## Crystal structure and Hirshfeld surface of a pentaamminecopper(II) complex with urea and chloride

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### Computing details

#### Pentaamminecopper(II) dichloride–urea (1/1)

##### Crystal data

[Cu(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub>·CH<sub>4</sub>N<sub>2</sub>O

*M<sub>r</sub>* = 279.67

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 12.2214 (2) Å

*b* = 7.0230 (1) Å

*c* = 13.0537 (3) Å

$\beta$  = 94.511 (2)°

*V* = 1116.94 (4) Å<sup>3</sup>

*Z* = 4

*F*(000) = 580

*D<sub>x</sub>* = 1.663 Mg m<sup>-3</sup>

Cu *K*α radiation,  $\lambda$  = 1.54184 Å

Cell parameters from 8370 reflections

$\theta$  = 4.8–66.6°

$\mu$  = 7.01 mm<sup>-1</sup>

*T* = 100 K

Block, blue

0.45 × 0.22 × 0.12 mm

##### Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.3196 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)

*T*<sub>min</sub> = 0.229, *T*<sub>max</sub> = 1.000

12732 measured reflections

1977 independent reflections

1835 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.059

$\theta_{\max}$  = 66.6°,  $\theta_{\min}$  = 4.8°

*h* = -14→14

*k* = -7→8

*l* = -15→15

##### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.033

*wR*(*F*<sup>2</sup>) = 0.092

*S* = 1.08

1977 reflections

130 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0515*P*)<sup>2</sup> + 1.0977*P*]

where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.67 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.80 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  | 0.58604 (3)  | 0.73373 (4) | 0.21577 (2)  | 0.00720 (15)                     |
| N12  | 0.48687 (15) | 0.9643 (3)  | 0.19244 (13) | 0.0121 (4)                       |
| H12A | 0.517997     | 1.048085    | 0.150183     | 0.015*                           |
| H12B | 0.477733     | 1.021555    | 0.253724     | 0.015*                           |
| H12C | 0.420444     | 0.926610    | 0.162954     | 0.015*                           |
| N15  | 0.46406 (15) | 0.5045 (3)  | 0.18411 (14) | 0.0127 (4)                       |
| H15A | 0.492053     | 0.415157    | 0.142989     | 0.015*                           |
| H15B | 0.401766     | 0.554421    | 0.151974     | 0.015*                           |
| H15C | 0.448160     | 0.449703    | 0.244330     | 0.015*                           |
| N11  | 0.58082 (18) | 0.7487 (3)  | 0.37130 (16) | 0.0133 (5)                       |
| H11A | 0.543429     | 0.855049    | 0.387772     | 0.016*                           |
| H11B | 0.650406     | 0.754010    | 0.401582     | 0.016*                           |
| H11C | 0.546287     | 0.643803    | 0.393945     | 0.016*                           |
| N13  | 0.61575 (18) | 0.7501 (2)  | 0.06366 (15) | 0.0137 (5)                       |
| H13A | 0.550830     | 0.753527    | 0.024449     | 0.016*                           |
| H13B | 0.654939     | 0.646477    | 0.046280     | 0.016*                           |
| H13C | 0.654659     | 0.857730    | 0.052718     | 0.016*                           |
| N14  | 0.71579 (15) | 0.5531 (3)  | 0.23815 (14) | 0.0169 (4)                       |
| H14A | 0.703349     | 0.447470    | 0.198543     | 0.020*                           |
| H14B | 0.724294     | 0.518588    | 0.305504     | 0.020*                           |
| H14C | 0.777763     | 0.612328    | 0.220417     | 0.020*                           |
| Cl31 | 0.85423 (5)  | 0.74020 (7) | 0.45789 (4)  | 0.01096 (18)                     |
| Cl41 | 0.91879 (5)  | 0.74644 (7) | 0.10532 (4)  | 0.01357 (18)                     |
| O23  | 0.25100 (15) | 0.7563 (2)  | 0.23770 (13) | 0.0139 (4)                       |
| N24  | 0.31771 (16) | 0.9190 (3)  | 0.37916 (15) | 0.0131 (4)                       |
| N21  | 0.30606 (17) | 0.5930 (3)  | 0.38261 (15) | 0.0140 (4)                       |
| C22  | 0.2895 (2)   | 0.7560 (3)  | 0.32963 (19) | 0.0089 (5)                       |
| H21A | 0.290 (2)    | 0.495 (4)   | 0.355 (2)    | 0.011 (7)*                       |
| H24A | 0.302 (2)    | 1.018 (5)   | 0.350 (2)    | 0.016 (7)*                       |
| H21B | 0.333 (2)    | 0.601 (4)   | 0.446 (2)    | 0.020 (7)*                       |
| H24B | 0.346 (2)    | 0.912 (5)   | 0.443 (2)    | 0.026 (8)*                       |

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

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Cu1 | 0.0095 (2)  | 0.0032 (2)  | 0.0089 (2)  | 0.00087 (11) | 0.00069 (14) | 0.00008 (10) |
| N12 | 0.0148 (9)  | 0.0080 (10) | 0.0138 (8)  | 0.0009 (8)   | 0.0024 (7)   | 0.0003 (7)   |
| N15 | 0.0150 (9)  | 0.0066 (10) | 0.0167 (9)  | −0.0004 (7)  | 0.0029 (7)   | −0.0011 (7)  |
| N11 | 0.0152 (11) | 0.0122 (12) | 0.0127 (10) | 0.0028 (7)   | 0.0020 (8)   | 0.0009 (6)   |

|      |             |             |             |               |             |              |
|------|-------------|-------------|-------------|---------------|-------------|--------------|
| N13  | 0.0154 (11) | 0.0123 (12) | 0.0138 (10) | 0.0016 (7)    | 0.0036 (8)  | -0.0002 (7)  |
| N14  | 0.0189 (9)  | 0.0114 (11) | 0.0201 (9)  | 0.0050 (8)    | -0.0009 (7) | -0.0008 (8)  |
| Cl31 | 0.0126 (3)  | 0.0075 (3)  | 0.0126 (3)  | -0.00014 (17) | 0.0000 (2)  | 0.00015 (17) |
| Cl41 | 0.0218 (3)  | 0.0075 (3)  | 0.0110 (3)  | 0.00044 (18)  | -0.0010 (2) | 0.00017 (17) |
| O23  | 0.0231 (10) | 0.0078 (10) | 0.0102 (8)  | 0.0021 (6)    | -0.0026 (7) | -0.0006 (5)  |
| N24  | 0.0235 (10) | 0.0031 (10) | 0.0122 (9)  | 0.0020 (8)    | -0.0025 (7) | 0.0002 (8)   |
| N21  | 0.0269 (11) | 0.0036 (10) | 0.0111 (9)  | -0.0021 (8)   | -0.0020 (7) | -0.0010 (8)  |
| C22  | 0.0086 (11) | 0.0057 (13) | 0.0130 (11) | 0.0017 (7)    | 0.0036 (9)  | -0.0008 (7)  |

*Geometric parameters (Å, °)*

|               |             |               |             |
|---------------|-------------|---------------|-------------|
| Cu1—N11       | 2.039 (2)   | N13—H13A      | 0.9100      |
| Cu1—N12       | 2.0313 (19) | N13—H13B      | 0.9100      |
| Cu1—N13       | 2.050 (2)   | N13—H13C      | 0.9100      |
| Cu1—N14       | 2.0339 (19) | N14—H14A      | 0.9100      |
| Cu1—N15       | 2.2107 (19) | N14—H14B      | 0.9100      |
| N12—H12A      | 0.9100      | N14—H14C      | 0.9100      |
| N12—H12B      | 0.9100      | O23—C22       | 1.254 (3)   |
| N12—H12C      | 0.9100      | N24—C22       | 1.346 (3)   |
| N15—H15A      | 0.9100      | N24—H24A      | 0.81 (3)    |
| N15—H15B      | 0.9100      | N24—H24B      | 0.87 (3)    |
| N15—H15C      | 0.9100      | N21—C22       | 1.344 (3)   |
| N11—H11A      | 0.9100      | N21—H21A      | 0.80 (3)    |
| N11—H11B      | 0.9100      | N21—H21B      | 0.87 (3)    |
| N11—H11C      | 0.9100      |               |             |
| N11—Cu1—N15   | 98.65 (7)   | H11A—N11—H11B | 109.5       |
| N12—Cu1—N15   | 99.60 (8)   | H11A—N11—H11C | 109.5       |
| N13—Cu1—N15   | 91.61 (7)   | H11B—N11—H11C | 109.5       |
| N14—Cu1—N15   | 94.55 (8)   | Cu1—N13—H13A  | 109.5       |
| N12—Cu1—N11   | 92.47 (7)   | Cu1—N13—H13B  | 109.5       |
| N12—Cu1—N13   | 87.65 (7)   | Cu1—N13—H13C  | 109.5       |
| N12—Cu1—N14   | 165.49 (8)  | H13A—N13—H13B | 109.5       |
| N11—Cu1—N13   | 169.57 (8)  | H13A—N13—H13C | 109.5       |
| N14—Cu1—N11   | 88.53 (8)   | H13B—N13—H13C | 109.5       |
| N14—Cu1—N13   | 88.78 (8)   | Cu1—N14—H14A  | 109.5       |
| Cu1—N12—H12A  | 109.5       | Cu1—N14—H14B  | 109.5       |
| Cu1—N12—H12B  | 109.5       | Cu1—N14—H14C  | 109.5       |
| Cu1—N12—H12C  | 109.5       | H14A—N14—H14B | 109.5       |
| H12A—N12—H12B | 109.5       | H14A—N14—H14C | 109.5       |
| H12A—N12—H12C | 109.5       | H14B—N14—H14C | 109.5       |
| H12B—N12—H12C | 109.5       | C22—N24—H24A  | 118 (2)     |
| Cu1—N15—H15A  | 109.5       | C22—N24—H24B  | 118 (2)     |
| Cu1—N15—H15B  | 109.5       | H24A—N24—H24B | 124 (3)     |
| Cu1—N15—H15C  | 109.5       | C22—N21—H21A  | 118.7 (19)  |
| H15A—N15—H15B | 109.5       | C22—N21—H21B  | 118 (2)     |
| H15A—N15—H15C | 109.5       | H21A—N21—H21B | 124 (3)     |
| H15B—N15—H15C | 109.5       | O23—C22—N24   | 121.39 (19) |



|              |       |             |             |
|--------------|-------|-------------|-------------|
| Cu1—N11—H11A | 109.5 | O23—C22—N21 | 121.60 (19) |
| Cu1—N11—H11B | 109.5 | N21—C22—N24 | 117.0 (2)   |
| Cu1—N11—H11C | 109.5 |             |             |

*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> |
|--------------------------------|-------------|---------------|-----------------------|-------------------------|
| N11—H11A...Cl41 <sup>i</sup>   | 0.91        | 2.79          | 3.509 (2)             | 137                     |
| N11—H11B...Cl31                | 0.91        | 2.54          | 3.443 (2)             | 170                     |
| N11—H11C...Cl41 <sup>ii</sup>  | 0.91        | 2.82          | 3.541 (2)             | 137                     |
| N12—H12A...Cl31 <sup>i</sup>   | 0.91        | 2.57          | 3.461 (2)             | 167                     |
| N12—H12B...Cl41 <sup>i</sup>   | 0.91        | 2.67          | 3.4273 (19)           | 142                     |
| N13—H13A...Cl31 <sup>iii</sup> | 0.91        | 2.49          | 3.381 (2)             | 166                     |
| N13—H13C...Cl31 <sup>i</sup>   | 0.91        | 2.69          | 3.4752 (15)           | 145                     |
| N14—H14A...Cl31 <sup>ii</sup>  | 0.91        | 2.56          | 3.430 (2)             | 160                     |
| N14—H14C...Cl41                | 0.91        | 2.55          | 3.418 (2)             | 159                     |
| N15—H15A...Cl31 <sup>ii</sup>  | 0.91        | 2.68          | 3.530 (2)             | 157                     |
| N21—H21A...O23 <sup>iv</sup>   | 0.79 (3)    | 2.11 (3)      | 2.893 (3)             | 172 (3)                 |
| N21—H21B...Cl41 <sup>v</sup>   | 0.87 (3)    | 2.50 (3)      | 3.315 (2)             | 158 (2)                 |
| N24—H24A...O23 <sup>vi</sup>   | 0.81 (3)    | 2.10 (3)      | 2.906 (3)             | 173 (3)                 |
| N24—H24B...Cl41 <sup>v</sup>   | 0.88 (3)    | 2.50 (3)      | 3.319 (2)             | 157 (3)                 |

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