The title Cu II macroyclic complex salt tetrahydrate, [Cu(C22H46N6O2)]-
(C2H3O2)2-4H2O, sees the metal atom located on a centre of inversion and
coordinated within a 4 + 2 (N4O2) tetragonally distorted coordination geometry;
the N atoms are derived from the macrocycle and the O atoms from weakly
associated [3.2048 (15) Å] acetate anions. Further stability to the three-ion
aggregate is provided by intramolecular amine-N—H/C1/C1/C1/C1O(carboxylate)
hydrogen bonds. Hydrogen bonding is also prominent in the molecular
packing with amide-N—H/C1/C1/C1/C1O(amide) interactions, leading to eight-
membered {/C1/C1/C1HNCO}2 synthons, amide-N—H/C1/C1/C1/C1O(water), water-O—
H/C1/C1/C1/C1O(carboxylate) and water-O—H/C1/C1/C1/C1O(water) hydrogen bonds featuring
within the three-dimensional architecture. The calculated Hirshfeld surfaces for
the individual components of the asymmetric unit differentiate the water
molecules owing to their distinctive supramolecular association. For each of the
anion and cation, H/C1/C1/C1/H contacts predominate (50.7 and 65.2%, respectively)
followed by H/C1/C1/C1/O/O contacts (44.5 and 29.9%, respectively).

1. Chemical context

Owing to the multifarious applications of different metal complexes of a wide variety of macrocyclic ligands (Ali et al., 2019; Bernhardt & Sharpe, 2000; Lamani et al., 2018; Vicente et al., 2003; Xu et al., 2020), studies on some N-pendent macrocyclic ligands and their metal complexes were described by us recently (Dey, Rabi, Hazari et al., 2021; Dey, Rabi, Palit et al., 2021). In a continuation of this work, a new N-pendent carbamoyl-derived macrocyclic ligand, ‘tet-am’, C22H46N6O2, prepared from ‘tet-a’ (an isomeric ligand of the hexamethyl tetrazamacroyclic ligand) and acrylamide has been synthesized, by employing the procedure described for the preparation of a related N-pendent ligand (Dey, Rabi, Hazari et al., 2021). Thereafter, the interaction of the new ‘tet-am’ ligand with copper(II) acetate monohydrate furnished violet crystals formulated as [Cu(tet-am)](O2CCH3)2-4H2O, hereafter (I). Herein, we describe the synthesis of (I), its analysis by single crystal X-ray diffraction and a detailed study of supramolecular association by an evaluation of the calculated Hirshfeld surfaces and two-dimensional fingerprint plots.
2. Structural commentary

The molecular structure diagram showing the complex dication and loosely associated anions is shown in Fig. 1. The Cu atom is located on a centre of inversion and is coordinated by tertiary and secondary N atoms with the bond length formed by the former, i.e. Cu—N2 = 2.0016 (12) Å, being approximately 0.1 Å shorter than the Cu—N1 bond of 2.1086 (11) Å. Whereas the conformation of the five-membered chelate ring is best described as being an envelope with the C4 atom being the flap atom, the six-membered chelate ring approximates a chair conformation. The acetate anions are weakly associated with the complex cation, forming relatively long Cu—O3 separations of 3.2048 (15) Å with extra stability to the three-ion aggregate provided by intramolecular amine-N—H—O(carboxylate) hydrogen bonds, Table 1. The coordination geometry for the Cu centre can therefore, be considered 4 + 2 N4O2 tetragonally distorted. From symmetry, the N1-bound carboxamoyethyl groups lie to opposite sides of the CuN4 plane and the N1—C9—C10—C11 torsion angle of −178.52 (12)° is consistent with an –anti-periplanar (–ap) configuration.

3. Supramolecular features

Conventional hydrogen bonding is prominent among the directional supramolecular contacts evident in the crystal of (I); Table 1 compiles a listing of these interactions. As mentioned above, the amine forms an intramolecular amine-N—H—O(carboxylate) hydrogen bond. The amide forms an amide-N—H—O(amide) hydrogen bond with a centrosymmetrically related molecule, via an eight-membered [···HNCO]3 synthon, and the second H atom participates in an amide-N—H—O(water) hydrogen bond. This water molecule, i.e. water-O1W, also forms donor interactions to a...
Two views of the Hirshfeld surface for the O2 water molecule of (I) over \( d_{\text{norm}} \) highlighting (a) O2W–H1W···O(carbonyl/carboxylate) hydrogen bonds and (b) the O1W–H1W···O2W hydrogen bond.

Figure 4

Two views of the Hirshfeld surface for the O2 water molecule of (I) over \( d_{\text{norm}} \) highlighting (a) O2W–H1W···O(carbonyl/carboxylate) hydrogen bonds and (b) the O1W–H1W···O2W hydrogen bond.

Carboxylate–O2 atom and to the second water molecule, i.e. water–O2W. The latter forms donor interactions with the amide–O and carboxylate–O3 atoms. As can be seen from the unit-cell diagram of Fig. 2, globally, the three-ion aggregates align in chains along the \( a \) axis direction with the prominent hydrogen bonds between the molecules in that direction being water–O–H···O(water) and water–O–H···O3(carboxylate). The remaining hydrogen bonds extend laterally to consolidate the three-dimensional supramolecular network.

4. Analysis of the Hirshfeld surfaces

The Hirshfeld surface analysis for each constituent of (I) was performed to provide further information on the supramolecular connections in the crystal and to differentiate the modes of association of the water molecules. The calculated Hirshfeld surfaces were mapped over the normalized contact

| Contact | Distance | Symmetry operation |
|---------|----------|--------------------|
| O1W–H1W···O2W | 1.83 | \( x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2} \) |
| O1W–H2W···O2W | 1.79 | \( x, y, z \) |
| N3–H2W···O1W | 2.03 | \(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}\) |
| O2W–H3W···O3 | 1.81 | \( x, y, z \) |
| O2W–H4W···O1W | 1.90 | \(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}\) |
| N2–H1N···O2 | 1.86 | \(-x + 1, -y + 1, -z + 1\) |
| N3–H3W···O1 | 2.22 | \(-x + 1, -y + 2, -z + 1\) |
| C5–H5A···O1W | 2.38 | \(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}\) |
| C7–H7B···O1W | 2.45 | \( x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}\) |
| C8–H8C···O1W | 2.48 | \(-x + 1, -y + 1, -z + 1\) |
| C4–H4A···O3 | 2.35 | \( x, y, z \) |
| C7–H7A···O3 | 2.26 | \( x, y, z \) |
| H7C–H10A | 2.14 | \(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}\) |

Notes: (a) The interatomic distances are calculated in Crystal Explorer 17 (Turner et al., 2017) with the \( X–H \) bond lengths adjusted to their neutron values. (b) The interaction corresponds to a conventional hydrogen bond (compare Table 1).

As a hydrogen-bond donor, the two bright red spots on the \( d_{\text{norm}} \)-Hirshfeld surface of the O1W water molecule are due to the formation of conventional water–O–H···O(water) and water–O–H···O(carbonyl/oxalate) hydrogen bonds, Fig. 3(a). The other bright-red spot appearing on the \( d_{\text{norm}} \)-Hirshfeld surface is due to the formation of a conventional primary amide–N–H···O(water) hydrogen bond, Fig. 3(b). Further, weak methylene/methyl–C–H···O(water) interactions are also shown as faint red spots near atoms H5A, H7B and H8C in Fig. 3(b). Similar to the O1W-water molecule, the two O2W–H atoms participate in conventional water–O–H···O(carbonyl/oxalate) and water–O–H···O(amide) hydrogen bonds. These hydrogen bonds are manifested as two bright-red spots on the \( d_{\text{norm}} \)-Hirshfeld surface of the O2W molecule, Fig. 4(a). The third bright red spot, evident in Fig. 4(b), is due to the water–O–H···O(water) hydrogen bond as discussed above.

For the carboxylate anion, the bright-red spots on its \( d_{\text{norm}} \)-Hirshfeld surface correspond to the water–O–H···O(carbonyl/oxalate) hydrogen bonds, Fig. 5(a); the amide–N–H···O(carbonyl/oxalate) hydrogen bond, which also leads to a bright-red spot, is highlighted in Fig. 5(b). At the same time, the weak methylene–H4A/methyl–H7A···O3(carbonyl/oxalate) interaction distance \( d_{\text{norm}} \) (Spackman & Jayatilaka, 2009). These along with the associated two-dimensional fingerprint plots (Spackman & McKinnon, 2002) were calculated with Crystal Explorer 17 (Turner et al., 2017) following literature precedents (Tan et al., 2019). The colour for the \( d_{\text{norm}} \) surface was scaled between −0.621 (blue) and 1.131 a.u. (red). Key interatomic parameters are listed in Table 2.
interactions, with separations of 0.38 and 0.47 Å shorter than the sum of van der Waals radii, respectively, are shown as faint red spots in Fig. 5(b).

On the $d_{\text{norm}}$-Hirshfeld surface calculated for the cation, the bright-red spots near the amide-O1, methyl-H7A, amine-H1N and amide-H2N atoms, Fig. 6, arise from interactions mentioned above.

The amide-N–H⋯O(amide) hydrogen bond, which serves to link cations, is shown as bright-red spots near the amide-O1 and amide-H3N atoms in Fig. 7(a). Especially highlighted in Fig. 7(b) is a short H7C⋯H10A contact, reflected as a faint-red spot on the $d_{\text{norm}}$-Hirshfeld surface, with a separation of 2.14 Å, which is 0.26 Å shorter than sum of the van der Waals radii.

In order to quantify the interatomic contacts for each individual species comprising the asymmetric-unit, the two-dimensional fingerprint plots were also generated. The overall fingerprint plot and those delineated into H⋯H, H⋯O/O⋯H, H⋯C/C⋯H and H⋯N/N⋯H surface contacts are illustrated in Fig. 8, and the percentage contributions of the delineated contacts are tabulated in Table 3. As each water molecule only interacts with hydrogen and oxygen atoms, their two-dimensional fingerprint plot are saturated by H⋯H and H⋯O/O⋯H contacts. For the O1W-molecule, the H⋯H and H⋯O/O⋯H contacts contribute 47.6 and 52.4% to the Hirshfeld surface, respectively. On account of the C–H⋯O and N–H⋯O interactions evinced for the O1W-molecule, the contribution of H⋯H and H⋯O/O⋯H contacts differ by ~2% as compared to the near equal contributions for the O2W-molecule (H⋯H = 49.8%; H⋯O/O⋯H = 50.2%), which does not form analogous contacts.

The most significant intermolecular contacts involving the anion are the H⋯H and H⋯O/O⋯H contacts; these contacts tipped at $d_+ = d_1 \sim 2.2$ Å and $d_+ + d_1 \sim 1.8$ Å, respectively, Fig. 8. The H⋯H contacts contribute 50.7% to the overall Hirshfeld surface of the anion, while the H⋯O/O⋯H contribute 44.5%, Table 3. The next most significant

Table 3
A summary of the percentage contributions to the calculated Hirshfeld surfaces for the individual constituents of (I).

| Contact | Water-O1W | Water-O2W | Anion | Cation |
|---------|-----------|-----------|-------|--------|
| H⋯H    | 47.6      | 49.8      | 50.7  | 65.2   |
| H⋯O/O⋯H| 52.4      | 50.2      | 44.5  | 29.9   |
| H⋯C/C⋯H| –         | –         | 4.2   | 2.8    |
| H⋯N/N⋯H| –         | –         | 0.3   | 2.0    |
| C⋯Cu/Cu⋯C| –      | –         | 0.3   | 0.1    |

Figure 5
Two views of the Hirshfeld surface for the anion in (I) over $d_{\text{norm}}$ highlighting (a) conventional hydrogen bonds and (b) C–H⋯O interactions.

Figure 6
A view of the Hirshfeld surface for the cation in (I) over $d_{\text{norm}}$.

Figure 7
Two views of the Hirshfeld surface for the cation in (I) over $d_{\text{norm}}$ highlighting (a) amide-N–H⋯O(amide) hydrogen bonds and (b) H⋯H interactions.
interatomic contacts are $\text{H} \cdots \text{C} \cdots \text{H}$ contacts, but these only contribute 4.2% to the overall Hirshfeld surface. Consistent with the loose association between the anion and cation, the $\text{O} \cdots \text{Cu} \cdots \text{O}$ contacts only contribute 0.3% to the overall Hirshfeld surface, Table 3.

For the cation, $\text{H} \cdots \text{H}$ contacts contribute 65.2% to the overall Hirshfeld surface with the shortest contact, manifested in the beak-like peak tipped at $d_e = d_i \sim 2.2$ Å, Fig. 8, corresponding to the $\text{H7C} \cdots \text{H10A}$ contact listed in Table 2. The $\text{H} \cdots \text{O} \cdots \text{O} \cdots \text{H}$ contacts contribute 29.9% to the surface reflecting the conventional hydrogen bonds that involve water, acetate and carbamoylethyl moieties, as discussed above. The shortest $\text{H} \cdots \text{O} \cdots \text{O} \cdots \text{H}$ contacts are reflected as two sharp spikes at $d_e = d_i \sim 1.9$ Å in Fig. 8. Even through both $\text{H} \cdots \text{C}$
C⋯H and H⋯N/N⋯H contacts appear in the two-dimensional fingerprint plots of the cation, their contributions to the overall Hirshfeld surface are only 2.8 and 2.0%, respectively. As observed for the anion, the weak connection between the CuII centre and the carboxylate ligand is reflected in a very low contribution of O⋯Cu/Cu⋯O contacts (0.1%) to the overall Hirshfeld surface of the cation.

5. Database survey

There are two relevant structures in the literature available for comparison having closely related 14-membered tetraaza macrocycles bearing two pendent N-bound CH\_2CH\_2CONH\_2 arms (Kang et al., 2008). These structures present very different coordination geometries to each other and to that of (I). The common feature of the literature structures is the presence of perchlorate counter-anions, which do not coordinate the Cu\(^{II}\) atom in either case. Rather, the amide-O atom of one side-arm folds over the molecule to form a Cu—O bond. In the C-rac-macrocyclic complex, a square-pyramidal geometry ensues with the amide-O atom [2.207 (4) Å] occupying the apical position. While the trans-orientated Cu—N(tertiary) bond lengths of 2.083 (4) and 2.086 (4) Å are longer than Cu—N(secondary) bonds of 2.035 (4) and 2.045 (4) Å, the differences between the short and long bond lengths are not as great as noted above for (I). In the structure with the configurational C-meso isomer, the coordination geometry changes to trigonal-bipyramidal with the amide-O atom occupying an equatorial position, forming a significantly shorter Cu—O bond length [2.007 (4) Å] compared to that in the racemic isomer. The tertiary-N atoms occupy axial positions and form Cu—N(secondary) bond lengths of 2.063 (4) and 2.083 (4) Å, the differences between the short and long bond lengths are not as great as noted above for (I).

6. Synthesis and crystallization

**Synthesis of N-carbamoyethyl pendent derivative (tet-am):** The isomeric ligand, tet-a (0.320 g, 1.0 mmol), dissolved in hot methanol (50 ml), and acrylamide (0.28 g, 4.0 mmol), taken in a minimum amount of hot methanol, were mixed. The reaction mixture was refluxed for about 12 h, cooled to room temperature, filtered and allowed to stand for three days to evaporate slowly. The white product that formed, tet-am, was separated by filtration, washed with methanol followed by water and finally dried in a desiccator over silica gel; m.p. 378 K.

[Chemical formula: \(\text{[Cu(C}_2\text{H}_4\text{N}_4\text{O}_4](C}_2\text{H}_3\text{O}_2)\_2\cdot4\text{H}_2\text{O}\)]

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The carbon-bound H atoms were treated as riding with C—H = 0.96–0.98 Å and stored in a vacuum desiccator. Some violet crystals suitable for X-ray analysis were collected from the mother liquor (ethanol + diethyl ether) during the isolation of the complex; m.p. 378 K.

**Funding information**

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Table 4

| Crystal data | Chemical formula | \([\text{Cu(C}_2\text{H}_4\text{N}_4\text{O}_4](\text{C}_2\text{H}_3\text{O}_2)\_2\cdot4\text{H}_2\text{O})\] |
| --- | --- | --- |
| **M**<sub>r</sub> | 680.34 | 1.2 |
| Crystal system, space group | Monoclinic, \(P2_1/n\) | 0.029, 0.082, 1.05 |
| Temperature (K) | 298 | 3022, 2902 |
| \(a, b, c\) (Å) | 8.5733 (1), 14.2616 (2), 13.9853 (1) | 0.029, 0.082, 1.05 |
| \(\beta\) (°) | 97.525 (1) | 3022 |
| \(V\) (Å³) | 1695.24 (3) | 9 |
| \(Z\) | 2 | 1.05 |
| Radiation type | Cu Kα | 0.27, –0.57 |
| \(\mu\) (mm\(^{-1}\)) | 1.41 | 0.597 |
| Crystal size (mm) | 0.13 × 0.10 × 0.09 | 0.597 |

**Data collection**

Diffractometer | XtaLAB Synergy, Dualflex, AtlasS2 |
| --- | --- |
| Absorption correction | Gaussian (CrysAlis PRO; Rigaku OD, 2018) |
| \(T_{\text{min}}, T_{\text{max}}\) | 0.759, 1.000 |
| No. of measured, independent and observed \(|F| > 2\sigma(F)\) reflections | 21762, 3022, 2902 |
| \(R_{\text{free}}, R_{\text{free}}\) | 0.021, 0.029, 0.082 |
| No. of parameters | 3022 |
| No. of restraints | 221 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| \(\Delta \rho_{\text{free}}, \Delta \rho_{\text{free}}\) (e Ǻ\(^{-3}\)) | 0.27, –0.57 |

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**Computer programs:** CrysAlis PRO (Rigaku OD, 2018), SHELXL (Sheldrick, 2015a), SHELXL2016/3 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2000) and public CIF (Westrip, 2010).
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[rac-1,8-Bis(2-carbamoylethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) diacetate tetrahydrate: crystal structure and Hirshfeld surface analysis

Sabina Yasmin, Saswata Rabi, Avijit Chakraborty, Huey Chong Kwong, Edward R. T. Tiekink and Tapashi Ghosh Roy

Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2018); cell refinement: CrysAlis PRO (Rigaku OD, 2018); data reduction: CrysAlis PRO (Rigaku OD, 2018); program(s) used to solve structure: SHELXS (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012), DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

[rac-1,8-Bis(2-carbamoylethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) diacetate tetrahydrate

Crystal data

\[\text{Cu(C}_{22}\text{H}_{46}\text{N}_{6}\text{O}_{2})\left(\text{C}_{2}\text{H}_{3}\text{O}_{2}\right)_{2}\cdot4\text{H}_{2}\text{O}\]

\(M_r = 680.34\)

Monoclinic, \(P2_1/n\)

\(a = 8.5733 (1) \text{ Å}\)

\(b = 14.2616 (2) \text{ Å}\)

\(c = 13.9853 (1) \text{ Å}\)

\(\beta = 97.525 (1)^\circ\)

\(V = 1695.24 (3) \text{ Å}^3\)

\(Z = 2\)

\(F(000) = 734\)

\(D_x = 1.333 \text{ Mg m}^{-3}\)

Cu \(K\alpha\) radiation, \(\lambda = 1.54184 \text{ Å}\)

Cell parameters from 15564 reflections

\(\theta = 4.5–76.7^\circ\)

\(\mu = 1.41 \text{ mm}^{-1}\)

\(T = 298 \text{ K}\)

Prism, violet

0.13 \times 0.10 \times 0.09 \text{ mm}

Data collection

XtaLAB Synergy, Dualflex, AtlasS2 diffractometer

Detector resolution: 5.2558 pixels mm\(^{-1}\)

\(\omega\) scans

Absorption correction: gaussian

(CrysAlis PRO; Rigaku OD, 2018)

\(T_{\text{min}} = 0.759, T_{\text{max}} = 1.000\)

21762 measured reflections

3022 independent reflections

2902 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.021\)

\(\theta_{\text{max}} = 67.1^\circ, \theta_{\text{min}} = 4.5^\circ\)

\(h = -10\rightarrow10\)

\(k = -17\rightarrow15\)

\(l = -16\rightarrow16\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R(F^2 > 2\sigma(F^2)) = 0.029\)

\(wR(F^2) = 0.082\)

\(S = 1.05\)

3022 reflections

221 parameters

9 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

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     | Uiso*/Ueq |
|----------|-------|-------|-------|-----------|
| Cu       | 0.500000 | 0.500000 | 0.500000 | 0.02360 (11) |
| O1       | 0.43622 (17) | 0.90346 (9) | 0.40245 (9) | 0.0489 (3) |
| N1       | 0.33373 (13) | 0.59384 (8) | 0.42865 (8) | 0.0240 (3) |
| N2       | 0.62472 (15) | 0.49154 (8) | 0.38892 (9) | 0.0247 (3) |
| H1N      | 0.6690 (19) | 0.5461 (8) | 0.3906 (12) | 0.030* |
| N3       | 0.3815 (2) | 0.90050 (11) | 0.55447 (11) | 0.0467 (4) |
| H2N      | 0.336 (2) | 0.8725 (14) | 0.5972 (13) | 0.056* |
| H3N      | 0.424 (2) | 0.9545 (10) | 0.5645 (16) | 0.056* |
| C1       | 0.28843 (18) | 0.56941 (11) | 0.32369 (11) | 0.0306 (3) |
| H1       | 0.242073 | 0.506533 | 0.322290 | 0.037* |
| C2       | 0.4283 (2) | 0.56331 (11) | 0.26753 (10) | 0.0321 (3) |
| H2A      | 0.489347 | 0.620338 | 0.279548 | 0.039* |
| H2B      | 0.388224 | 0.562360 | 0.199376 | 0.039* |
| C3       | 0.54004 (19) | 0.48013 (10) | 0.28817 (10) | 0.0280 (3) |
| C4       | 0.19566 (17) | 0.57681 (11) | 0.48095 (11) | 0.0300 (3) |
| H4A      | 0.148419 | 0.516840 | 0.461466 | 0.036* |
| H4B      | 0.117429 | 0.625285 | 0.464338 | 0.036* |
| C5       | 0.24546 (18) | 0.57697 (11) | 0.58791 (11) | 0.0316 (3) |
| C6       | 0.1631 (2) | 0.63392 (15) | 0.26975 (13) | 0.0509 (5) |
| H6A      | 0.079754 | 0.643442 | 0.308328 | 0.076* |
| H6B      | 0.121476 | 0.605451 | 0.209592 | 0.076* |
| H6C      | 0.209854 | 0.693189 | 0.257616 | 0.076* |
| C7       | 0.4507 (2) | 0.38741 (11) | 0.27926 (12) | 0.0375 (4) |
| H7A      | 0.391849 | 0.380632 | 0.332703 | 0.056* |
| H7B      | 0.524106 | 0.336540 | 0.279424 | 0.056* |
| H7C      | 0.380039 | 0.386682 | 0.220060 | 0.056* |
| C8       | 0.6593 (2) | 0.48262 (13) | 0.21532 (13) | 0.0421 (4) |
| H8A      | 0.604261 | 0.482721 | 0.150975 | 0.063* |
| H8B      | 0.726044 | 0.428407 | 0.224151 | 0.063* |
| H8C      | 0.722305 | 0.538298 | 0.225308 | 0.063* |
| C9       | 0.40326 (17) | 0.68993 (10) | 0.44700 (10) | 0.0265 (3) |
| H9A      | 0.468591 | 0.703235 | 0.397011 | 0.032* |
|   | $u_{11}$  | $u_{22}$  | $u_{33}$  | $u_{12}$  | $u_{13}$  | $u_{23}$  |
|---|----------|----------|----------|----------|----------|----------|
| Cu | 0.02688 (18) | 0.02365 (18) | 0.02075 (17) | 0.00575 (11) | 0.00493 (12) | 0.00138 (10) |
| O1 | 0.0774 (9) | 0.0367 (7) | 0.0346 (6) | -0.0117 (6) | 0.0152 (6) | -0.0025 (5) |
| N1 | 0.0245 (6) | 0.0231 (6) | 0.0242 (6) | 0.0023 (5) | 0.0019 (5) | -0.0001 (5) |
| N2 | 0.0294 (7) | 0.0208 (6) | 0.0246 (6) | 0.0000 (5) | 0.0061 (5) | -0.0008 (5) |
| N3 | 0.0684 (11) | 0.0400 (9) | 0.0332 (8) | -0.0110 (8) | 0.0125 (7) | -0.0059 (6) |
| C1 | 0.0347 (8) | 0.0287 (8) | 0.0262 (7) | 0.0022 (6) | -0.0044 (6) | -0.0041 (6) |
| C2 | 0.0471 (9) | 0.0279 (8) | 0.0210 (7) | 0.0026 (7) | 0.0028 (6) | 0.0010 (6) |
| C3 | 0.0393 (8) | 0.0244 (7) | 0.0210 (7) | -0.0010 (6) | 0.0064 (6) | -0.0023 (6) |
| C4 | 0.0240 (7) | 0.0282 (8) | 0.0381 (8) | 0.0019 (6) | 0.0048 (6) | 0.0019 (6) |
| C5 | 0.0309 (8) | 0.0312 (8) | 0.0349 (8) | 0.0060 (6) | 0.0124 (6) | 0.0013 (6) |
| C6 | 0.0510 (11) | 0.0608 (12) | 0.0353 (9) | 0.0186 (9) | -0.0148 (8) | -0.0050 (8) |
| C7 | 0.0434 (9) | 0.0276 (8) | 0.0404 (9) | -0.0035 (7) | 0.0013 (7) | -0.0061 (7) |
| C8 | 0.0525 (9) | 0.0403 (9) | 0.0267 (9) | 0.0007 (8) | 0.0195 (8) | -0.0022 (7) |
| C9 | 0.0287 (8) | 0.0323 (7) | 0.0273 (7) | 0.0010 (6) | 0.0016 (5) | -0.0012 (6) |
| C10 | 0.0358 (8) | 0.0258 (8) | 0.0423 (9) | 0.0045 (6) | 0.0000 (7) | -0.0005 (7) |
| C11 | 0.0404 (8) | 0.0246 (8) | 0.0320 (8) | 0.0054 (6) | 0.0023 (6) | 0.0006 (6) |
| O2 | 0.0673 (8) | 0.0461 (7) | 0.0352 (7) | -0.0002 (6) | 0.0081 (5) | 0.0009 (5) |
| O3 | 0.0346 (10) | 0.0454 (8) | 0.0314 (7) | -0.0087 (10) | 0.0043 (5) | 0.0003 (5) |
| C12 | 0.0297 (8) | 0.0353 (8) | 0.0347 (8) | -0.0028 (6) | 0.0024 (6) | 0.0019 (7) |
| C13 | 0.0832 (16) | 0.0387 (11) | 0.0644 (13) | -0.0094 (10) | 0.0066 (12) | -0.0019 (10) |
| O1W | 0.0482 (8) | 0.0596 (7) | 0.0381 (7) | 0.0022 (6) | 0.0169 (6) | 0.0080 (5) |
| O2W | 0.0490 (9) | 0.0292 (12) | 0.0417 (8) | -0.0011 (8) | 0.0049 (6) | 0.0076 (8) |
### Geometric parameters (Å, °)

| Bond/Angle | Distance/Angle | Distance/Angle |
|------------|----------------|----------------|
| Cu—N2     | 2.0016 (12)    | C5—H5B 0.9700 |
| Cu—N2'    | 2.0016 (12)    | C6—H6A 0.9600 |
| Cu—N1     | 2.1086 (11)    | C6—H6B 0.9600 |
| Cu—N1'    | 2.1086 (11)    | C6—H6C 0.9600 |
| O1—C11    | 1.232 (2)      | C7—H7A 0.9600 |
| N1—C4     | 1.4906 (18)    | C7—H7B 0.9600 |
| N1—C9     | 1.5031 (18)    | C7—H7C 0.9600 |
| N1—C1     | 1.5092 (18)    | C8—H8A 0.9600 |
| N2—C5'    | 1.4846 (19)    | C8—H8B 0.9600 |
| N2—C3     | 1.5070 (19)    | C8—H8C 0.9600 |
| N2—H1N    | 0.864 (9)      | C9—C10 1.535 (2) |
| N3—C11    | 1.323 (2)      | C9—H9A 0.9700 |
| N3—H2N    | 0.854 (10)     | C9—H9B 0.9700 |
| N3—H3N    | 0.857 (10)     | C10—C11 1.519 (2) |
| C1—C2     | 1.519 (2)      | C10—H10A 0.9700 |
| C1—C6     | 1.535 (2)      | C10—H10B 0.9700 |
| C1—H1     | 0.9800         | O2—C12 1.247 (2) |
| C2—C3     | 1.529 (2)      | O3—C12 1.243 (2) |
| C2—H2A    | 0.9700         | C12—C13 1.506 (3) |
| C2—H2B    | 0.9700         | C13—H13A 0.9600 |
| C3—C7     | 1.525 (2)      | C13—H13B 0.9600 |
| C3—C8     | 1.536 (2)      | C13—H13C 0.9600 |
| C4—C5     | 1.501 (2)      | O1W—H1W 0.827 (9) |
| C4—H4A    | 0.9700         | O1W—H2W 0.828 (9) |
| C4—H4B    | 0.9700         | O2W—H3W 0.827 (10) |
| C5—H5A    | 0.9700         | O2W—H4W 0.823 (10) |

N2—Cu—N2'  180.0  N2'—C5—H5B  109.9
N2—Cu—N1   93.88 (5) C4—C5—H5B  109.9
N2—Cu—N1'  86.12 (5) H5A—C5—H5B  108.3
N2—Cu—N1   86.12 (5) C1—C6—H6A  109.5
N2—Cu—N1'  93.88 (5) C1—C6—H6B  109.5
N1—Cu—N1'  180.00 (5) H6A—C6—H6B  109.5
C4—N1—C9   112.80 (11) C1—C6—H6C  109.5
C4—N1—C1   108.65 (11) H6A—C6—H6C  109.5
C9—N1—C1   114.98 (11) H6B—C6—H6C  109.5
C4—N1—Cu   101.27 (8)  C3—C7—H7A  109.5
C9—N1—Cu   105.63 (8)  C3—C7—H7B  109.5
C1—N1—Cu   112.69 (8)  H7A—C7—H7B  109.5
C5—N2—C3   112.86 (11) C3—C7—H7C  109.5
C5—N2—Cu   109.37 (9)  H7A—C7—H7C  109.5
C3—N2—Cu   119.42 (9)  H7B—C7—H7C  109.5
C5—N2—H1N  105.8 (12)  C3—C8—H8A  109.5
C3—N2—H1N  106.2 (11)  C3—C8—H8B  109.5
Cu—N2—H1N  101.6 (11)  H8A—C8—H8B  109.5
C11—N3—H2N 119.9 (16)  C3—C8—H8C  109.5
C11—N3—H3N 117.7 (15)  H8A—C8—H8C 109.5
H2N—N3—H3N 122 (2)  H8B—C8—H8C 109.5
N1—C1—C2  113.33 (12)  N1—C9—C10  117.24 (12)
N1—C1—C6  114.45 (13)  N1—C9—H9A  108.0
C2—C1—C6  109.21 (14)  C10—C9—H9A  108.0
N1—C1—H1  106.4  N1—C9—H9B  108.0
C2—C1—H1  106.4  C10—C9—H9B  108.0
C6—C1—H1  106.4  H9A—C9—H9B  107.2
C1—C2—C3  117.68 (13)  C11—C10—C9  111.01 (13)
C1—C2—H2A  107.9  C11—C10—H10A  109.4
C3—C2—H2A  107.9  C9—C10—H10A  109.4
C1—C2—H2B  107.9  C11—C10—H10B  109.4
C3—C2—H2B  107.9  C9—C10—H10B  109.4
H2A—C2—H2B  107.2  H10A—C10—H10B  108.0
N2—C3—C7  110.20 (12)  O1—C11—N3  122.17 (16)
N2—C3—C2  107.82 (11)  O1—C11—C10  121.96 (14)
C7—C3—C2  111.22 (13)  N3—C11—C10  115.87 (15)
N2—C3—C8  109.67 (13)  O3—C12—O2  123.22 (16)
C7—C3—C8  109.68 (13)  O3—C12—C13  118.17 (16)
C2—C3—C8  108.20 (13)  O2—C12—C13  118.59 (16)
N1—C4—C5  110.38 (12)  C12—C13—H13A  109.5
N1—C4—H4A  109.6  C12—C13—H13B  109.5
C5—C4—H4A  109.6  H13A—C13—H13B  109.5
N1—C4—H4B  109.6  C12—C13—H13C  109.5
C5—C4—H4B  109.6  H13A—C13—H13C  109.5
H4A—C4—H4B  108.1  H13B—C13—H13C  109.5
N2—C5—C4  108.89 (12)  H1W—O1W—H2W  109.8 (16)
N2—C5—H5A  109.9  H3W—O2W—H4W  111.1 (16)
C4—C5—H5A  109.9

C4—N1—C1—C2  −167.31 (12)  C1—C2—C3—N2  −68.02 (17)
C9—N1—C1—C2  65.21 (15)  C1—C2—C3—C7  52.90 (18)
Cu—N1—C1—C2  −55.92 (14)  C1—C2—C3—C8  173.43 (13)
C4—N1—C1—C6  66.55 (17)  C9—N1—C4—C5  −65.30 (15)
C9—N1—C1—C6  −60.92 (18)  C1—N1—C4—C5  165.99 (12)
Cu—N1—C1—C6  177.94 (12)  Cu—N1—C4—C5  47.15 (12)
N1—C1—C2—C3  71.09 (17)  N1—C4—C5—N2i  −54.16 (16)
C6—C1—C2—C3  −160.03 (14)  C4—N1—C9—C10  40.36 (17)
C5—N2—C3—C7  67.35 (16)  C1—N1—C9—C10  84.99 (15)
Cu—N2—C3—C7  −63.28 (14)  Cu—N1—C9—C10  −150.11 (11)
C5—N2—C3—C2  −171.10 (12)  N1—C9—C10—C11  −178.52 (12)
Cu—N2—C3—C2  58.28 (14)  C9—C10—C11—O1  75.2 (2)
C5—N2—C3—C8  −53.49 (16)  C9—C10—C11—N3  −105.52 (17)
Cu—N2—C3—C8  175.88 (10)

Symmetry code: (i) −x+1, −y+1, −z+1.
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H  | H···A  | D···A   | D—H···A |
|---------|-------|--------|---------|---------|
| N2—H1N···O2\textsuperscript{i} | 0.87 (1) | 2.00 (1) | 2.8634 (18) | 173 (2) |
| N3—H2N···O1\textsuperscript{ii} | 0.85 (2) | 2.19 (2) | 3.031 (2) | 170 (2) |
| N3—H3N···O1\textsuperscript{iii} | 0.86 (2) | 2.37 (2) | 3.221 (2) | 175 (1) |
| O1\textsuperscript{W}—H2\textsuperscript{W}···O2 | 0.83 (1) | 1.94 (1) | 2.7574 (18) | 167 (2) |
| O1\textsuperscript{W}—H1\textsuperscript{W}···O2\textsuperscript{W} | 0.83 (2) | 1.98 (2) | 2.794 (2) | 167 (2) |
| O2\textsuperscript{W}—H3\textsuperscript{W}···O3 | 0.83 (2) | 1.96 (2) | 2.779 (2) | 169 (2) |
| O2\textsuperscript{W}—H4\textsuperscript{W}···O1\textsuperscript{v} | 0.82 (2) | 2.06 (2) | 2.869 (2) | 168 (2) |

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