



[*rac*-1,8-Bis(2-carbamoyl-ethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]-copper(II) diacetate tetrahydrate: crystal structure and Hirshfeld surface analysis

Sabina Yasmin,^a Saswata Rabi,^b Avijit Chakraborty,^a Huey Chong Kwong,^c Edward R. T. Tiekink^{c*} and Tapashi Ghosh Roy^{a‡}

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‡ Additional correspondence author, e-mail: tapashi57@cu.ac.bd.

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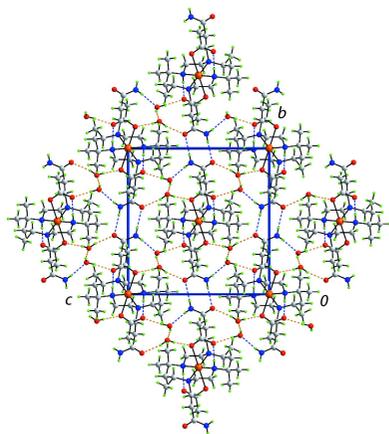
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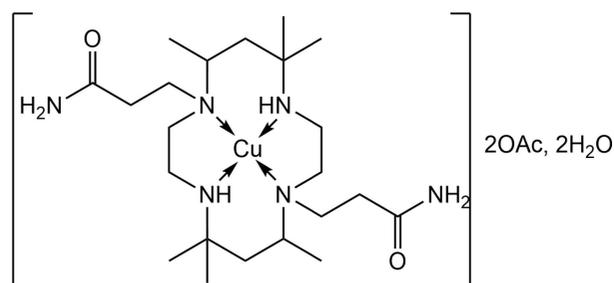
^aDepartment of Chemistry, University of Chittagong, Faculty of Science, Chattogram-4331, Bangladesh, ^bDepartment of Chemistry, Chittagong University of Engineering & Technology, Faculty of Engineering & Technology, Chattogram-4349, Bangladesh, and ^cResearch Centre for Crystalline Materials, School of Medical and Life Sciences, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia. *Correspondence e-mail: edwardt@sunway.edu.my

The title Cu^{II} macrocyclic 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···O(carboxylate) hydrogen bonds. Hydrogen bonding is also prominent in the molecular packing with amide-N—H···O(amide) interactions, leading to eight-membered {···HNCO}₂ synthons, amide-N—H···O(water), water-O—H···O(carboxylate) and water-O—H···O(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···H contacts predominate (50.7 and 65.2%, respectively) followed by H···O/O···H 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 tetrazamacrocyclic 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···(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

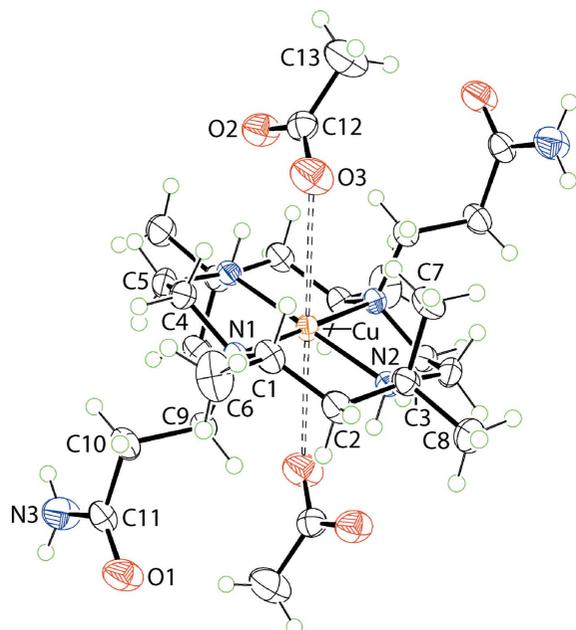


Figure 1

The molecular structure of the complex dication in (I) along with the loosely associated anions, showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. The molecule is disposed about an inversion centre with unlabelled atoms related by the symmetry operation $1 - x, 1 - y, 1 - z$. The weak Cu···O3 interactions above and below the CuN₄ plane are shown as dashed lines.

Table 1
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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N2–H1N···O2 ⁱ | 0.87 (1) | 2.00 (1) | 2.8634 (18) | 173 (2) |
| N3–H2N···O1W ⁱⁱ | 0.85 (2) | 2.19 (2) | 3.031 (2) | 170 (2) |
| N3–H3N···O1 ⁱⁱⁱ | 0.86 (2) | 2.37 (2) | 3.221 (2) | 175 (1) |
| O1W–H2W···O2 | 0.83 (1) | 1.94 (1) | 2.7574 (18) | 167 (2) |
| O1W–H1W···O2W ^{iv} | 0.83 (2) | 1.98 (2) | 2.794 (2) | 167 (2) |
| O2W–H3W···O3 | 0.83 (2) | 1.96 (2) | 2.779 (2) | 169 (2) |
| O2W–H4W···O1 ^v | 0.82 (2) | 2.06 (2) | 2.869 (2) | 168 (2) |

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

carbamoyl ethyl 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 {···HNCO₂}₂ 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

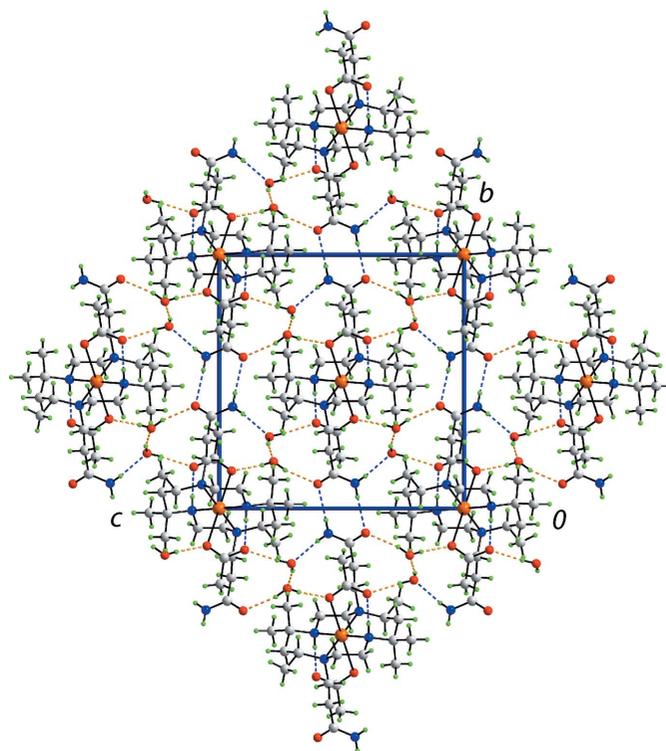


Figure 2

A view of the unit-cell contents of (I) shown in projection down the *a*-axis direction. The O–H···O and N–H···O hydrogen bonds are shown as orange and blue dashed lines, respectively.

Table 2

A summary of short interatomic contacts (Å) for (I)^a.

| Contact | Distance | Symmetry operation |
|----------------------------|----------|---|
| O1W—H1W...O2W ^b | 1.83 | $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ |
| O1W—H2W...O2 ^b | 1.79 | x, y, z |
| N3—H2N...O1W ^b | 2.03 | $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ |
| O2W—H3W...O3 ^b | 1.81 | x, y, z |
| O2W—H4W...O1 ^b | 1.90 | $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ |
| N2—H1N...O2 ^b | 1.86 | $-x + 1, -y + 1, -z + 1$ |
| N3—H3N...O1 ^b | 2.22 | $-x + 1, -y + 2, -z + 1$ |
| C5—H5A...O1W | 2.38 | $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ |
| 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).

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

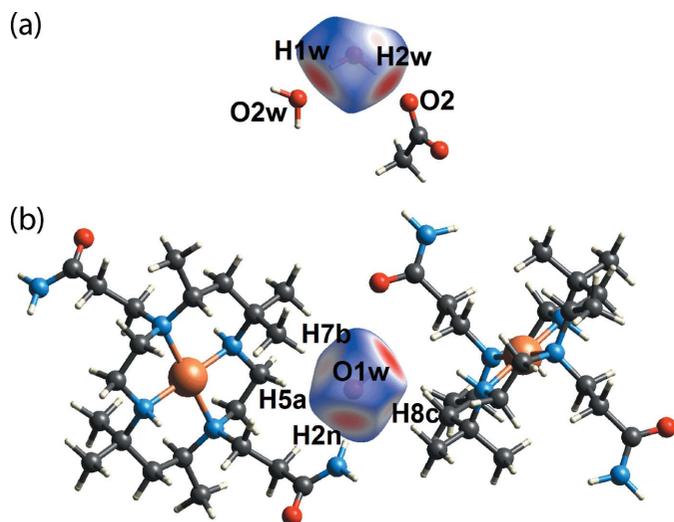


Figure 3

Two views of the Hirshfeld surface for the O1W-water molecule of (I) over d_{norm} highlighting (a) O1W—H...O(water/carboxylate) hydrogen bonds and (b) amide-N—H...O1W hydrogen bonds as well as weak C—H...O1W interactions.

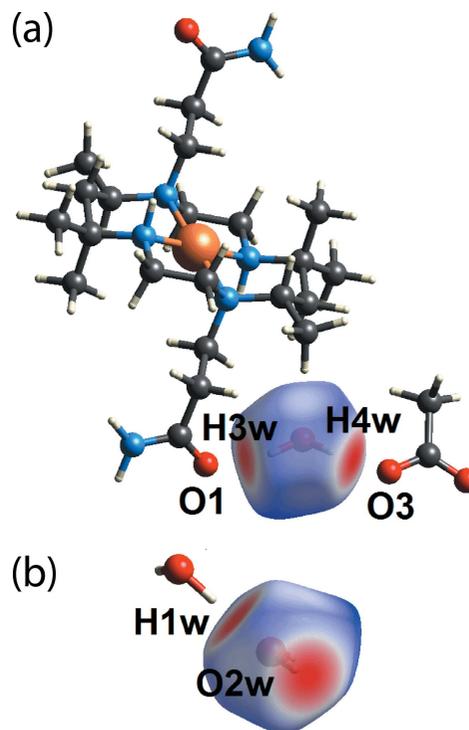


Figure 4

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

distance d_{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_{norm} surface was scaled between -0.621 (blue) and 1.131 a.u. (red). Key interatomic parameters are listed in Table 2.

As a hydrogen-bond donor, the two bright red spots on the d_{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(carboxylate) hydrogen bonds, Fig. 3(a). The other bright-red spot appearing on the d_{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(carboxylate) and water-O—H...O(water) hydrogen bonds. These hydrogen bonds are manifested as two bright-red spots on the d_{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_{norm} -Hirshfeld surface correspond to the water-O—H...O(carboxylate) hydrogen bonds, Fig. 5(a); the amide-N—H...O(carboxylate) 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(carboxylate)

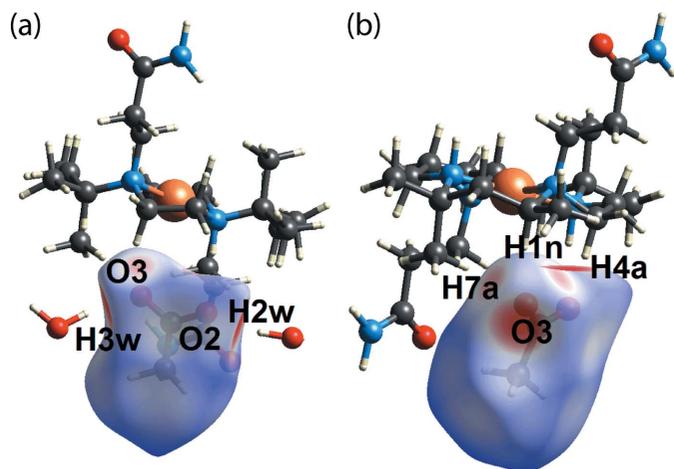


Figure 5
Two views of the Hirshfeld surface for the anion in (I) over d_{norm} highlighting (a) conventional hydrogen bonds and (b) C–H \cdots O interactions.

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_{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 \cdots 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 \cdots H10A contact, reflected as a faint-red spot on the d_{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

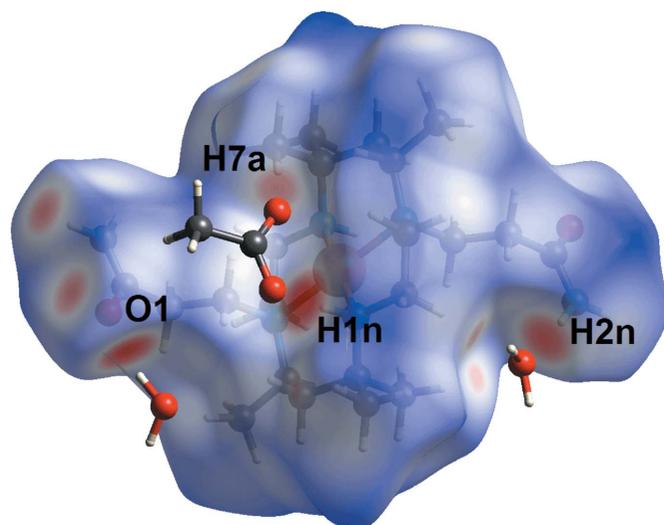


Figure 6
A view of the Hirshfeld surface for the cation in (I) over d_{norm} .

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 \cdots H | 47.6 | 49.8 | 50.7 | 65.2 |
| H \cdots O/O \cdots H | 52.4 | 50.2 | 44.5 | 29.9 |
| H \cdots C/C \cdots H | – | – | 4.2 | 2.8 |
| H \cdots N/N \cdots H | – | – | 0.3 | 2.0 |
| C \cdots Cu/Cu \cdots C | – | – | 0.3 | 0.1 |

fingerprint plot and those delineated into H \cdots H, H \cdots O/O \cdots H, H \cdots C/C \cdots H and H \cdots N/N \cdots 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 \cdots H and H \cdots O/O \cdots H contacts. For the O1W-molecule, the H \cdots H and H \cdots O/O \cdots H contacts contribute 47.6 and 52.4% to the Hirshfeld surface, respectively. On account of the C–H \cdots O and N–H \cdots O interactions evinced for the O1W-molecule, the contribution of H \cdots H and H \cdots O/O \cdots H contacts differ by \sim 2% as compared to the near equal contributions for the O2W-molecule (H \cdots H = 49.8%; H \cdots O/O \cdots H = 50.2%), which does not form analogous contacts.

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

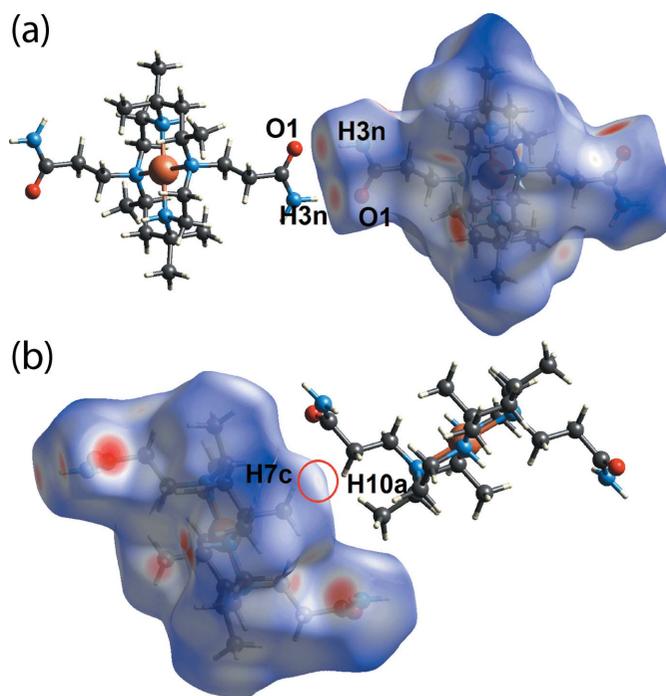


Figure 7
Two views of the Hirshfeld surface for the cation in (I) over d_{norm} highlighting (a) amide-N–H \cdots O(amide) hydrogen bonds and (b) H \cdots H interactions.

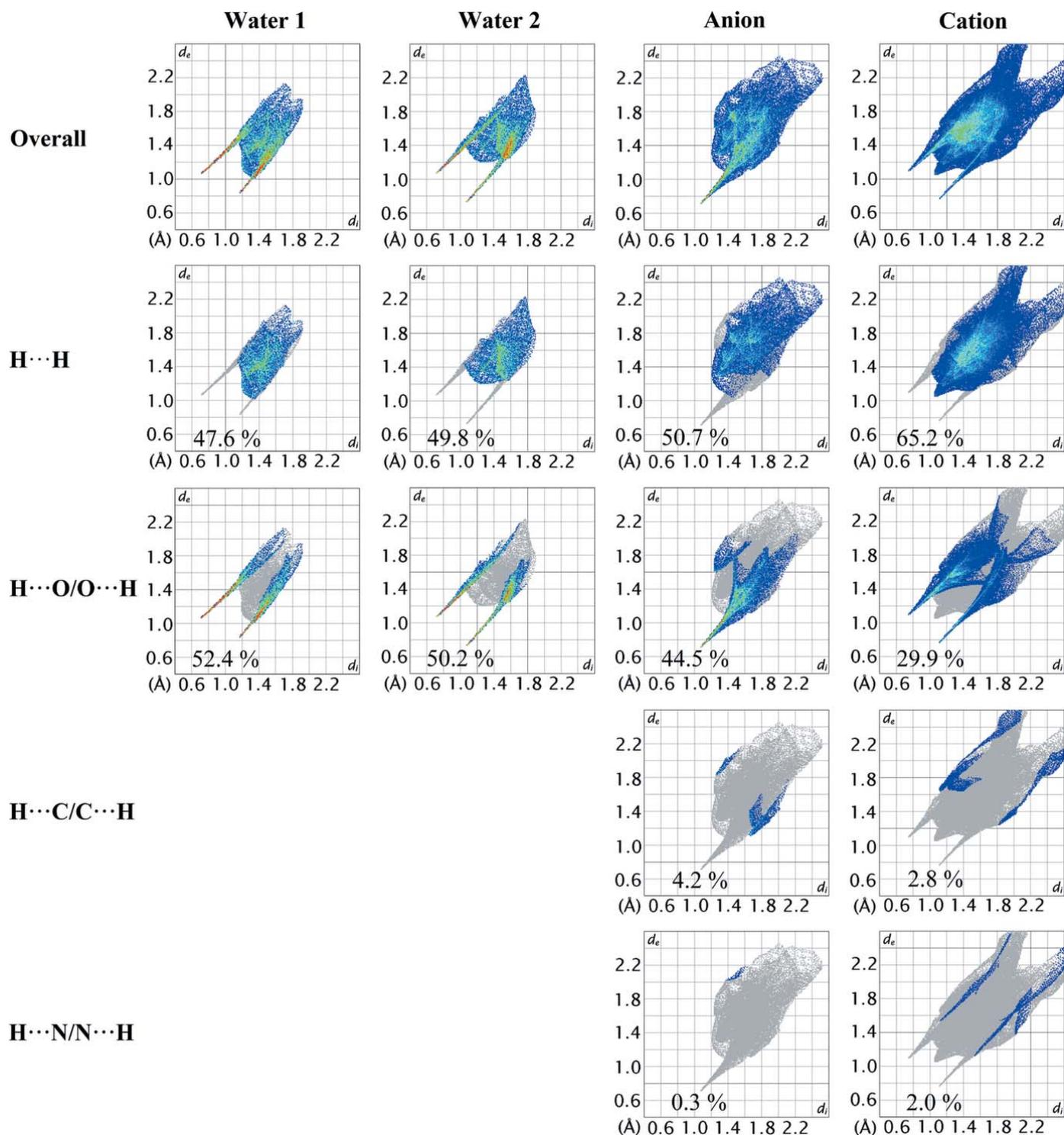


Figure 8

Overall two-dimensional fingerprint plots for each water molecule, anion and cation, and those delineated into H···H, H···O/O···H, H···C/C···H and H···N/N···H contacts.

interatomic contacts are H···C/C···H contacts, but these only contribute 4.2% to the overall Hirshfeld surface. Consistent with the loose association between the anion and cation, the O···Cu/Cu···O contacts only contribute 0.3% to the overall Hirshfeld surface, Table 3.

For the cation, H···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 H7C···H10A contact listed in Table 2. The H···O/O···H contacts contribute 29.9% to the surface reflecting the conventional hydrogen bonds that involve water, acetate and carbamoyl ethyl moieties, as discussed above. The shortest H···O/O···H contacts are reflected as two sharp spikes at $d_e = d_i \sim 1.9$ Å in Fig. 8. Even through both H···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 Cu^{II} 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 CH₂CH₂CONH₂ 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(tertiary) bond lengths of 2.063 (4) and 2.088 (4) Å which overlap with the Cu—N(secondary) bond lengths of 2.077 (4) and 2.090 (3) Å. The foregoing demonstrates a dependency of the Cu atom coordination geometry and the magnitudes of putative Cu to O interactions on the nature of the counter-anion and isomeric form of the ligand.

6. Synthesis and crystallization

Synthesis of *N*-carbamoylethyl 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. 458 K.

[Cu(tet-am)](O₂CCH₃)₂·4H₂O (I): The macrocycle, tet-am (0.426 g, 1.0 mmol) and copper(II) acetate monohydrate (0.199 g, 1.0 mmol) were dissolved separately in hot methanol (25 ml) and mixed while hot, resulting in an immediate colour change. The solution was heated on a steam-bath until the volume was reduced to less than 10 ml. After standing overnight, the sticky material that had formed was dissolved in a

Table 4
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | [Cu(C ₂₂ H ₄₆ N ₆ O ₂)](C ₂ H ₃ O ₂) ₂ ·4H ₂ O |
| <i>M_r</i> | 680.34 |
| Crystal system, space group | Monoclinic, <i>P</i> 2 ₁ / <i>n</i> |
| Temperature (K) | 298 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 8.5733 (1), 14.2616 (2), 13.9853 (1) |
| β (°) | 97.525 (1) |
| <i>V</i> (Å ³) | 1695.24 (3) |
| <i>Z</i> | 2 |
| Radiation type | Cu <i>K</i> α |
| μ (mm ⁻¹) | 1.41 |
| Crystal size (mm) | 0.13 × 0.10 × 0.09 |
| Data collection | |
| Diffractometer | XtaLAB Synergy, Dualflex, AtlasS2 |
| Absorption correction | Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2018) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.759, 1.000 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 21762, 3022, 2902 |
| <i>R</i> _{int} | 0.021 |
| (<i>sin</i> θ / λ) _{max} (Å ⁻¹) | 0.597 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.029, 0.082, 1.05 |
| No. of reflections | 3022 |
| No. of parameters | 221 |
| No. of restraints | 9 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 0.27, -0.37 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXS* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

minimum amount of ethanol followed by the addition of excess diethylether. The liquid portion was decanted and the remaining violet precipitate, (I), was dried over silica gel and stored in a vacuum desiccator. Some violet crystals suitable for X-ray analysis were collected from the mother liquor (ethanol + diethylether) during the isolation of the complex; m.p. 378 K.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The carbon-bound H atoms were placed in calculated positions (C—H = 0.96–0.98 Å) and were included in the refinement in the riding-model approximation, with *U*_{iso}(H) set to 1.2–1.5*U*_{eq}(C). The O- and N-bound H atoms were located in a difference-Fourier map and were refined with O—H = 0.82±0.01 and N—H = 0.86±0.01 Å distance restraints, and with *U*_{iso}(H) set to 1.5*U*_{eq}(O) and 1.2*U*_{eq}(N), respectively.

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supporting information

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

Crystal data

[Cu(C₂₂H₄₆N₆O₂)](C₂H₃O₂)₂·4H₂O
M_r = 680.34
 Monoclinic, *P*2₁/*n*
a = 8.5733 (1) Å
b = 14.2616 (2) Å
c = 13.9853 (1) Å
 β = 97.525 (1)°
V = 1695.24 (3) Å³
Z = 2

F(000) = 734
D_x = 1.333 Mg m⁻³
 Cu *K*α radiation, λ = 1.54184 Å
 Cell parameters from 15564 reflections
 θ = 4.5–76.7°
 μ = 1.41 mm⁻¹
T = 298 K
 Prism, violet
 0.13 × 0.10 × 0.09 mm

Data collection

XtaLAB Synergy, Dualflex, AtlasS2
 diffractometer
 Detector resolution: 5.2558 pixels mm⁻¹
 ω scans
 Absorption correction: gaussian
 (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min} = 0.759, *T_{max}* = 1.000
 21762 measured reflections

3022 independent reflections
 2902 reflections with *I* > 2σ(*I*)
R_{int} = 0.021
 θ_{\max} = 67.1°, θ_{\min} = 4.5°
h = -10→10
k = -17→15
l = -16→16

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*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

$$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.7827P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| 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) |
| H5A | 0.280725 | 0.639145 | 0.608960 | 0.038* |
| H5B | 0.157198 | 0.559990 | 0.621238 | 0.038* |
| 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* |

| | | | | |
|------|--------------|--------------|--------------|------------|
| H9B | 0.471905 | 0.688257 | 0.507891 | 0.032* |
| C10 | 0.28820 (19) | 0.77189 (11) | 0.45057 (12) | 0.0351 (4) |
| H10A | 0.217963 | 0.774789 | 0.390345 | 0.042* |
| H10B | 0.224957 | 0.761536 | 0.502257 | 0.042* |
| C11 | 0.37579 (19) | 0.86430 (11) | 0.46701 (11) | 0.0325 (3) |
| O2 | 0.20199 (16) | 0.33641 (9) | 0.60394 (9) | 0.0456 (3) |
| O3 | 0.21974 (19) | 0.35212 (10) | 0.44993 (9) | 0.0552 (4) |
| C12 | 0.19402 (18) | 0.30430 (12) | 0.52047 (11) | 0.0332 (3) |
| C13 | 0.1550 (3) | 0.20209 (15) | 0.50445 (17) | 0.0624 (6) |
| H13A | 0.096896 | 0.193856 | 0.441527 | 0.094* |
| H13B | 0.092734 | 0.180918 | 0.552479 | 0.094* |
| H13C | 0.250589 | 0.166327 | 0.509114 | 0.094* |
| O1W | 0.25081 (16) | 0.28246 (9) | 0.79485 (9) | 0.0454 (3) |
| H1W | 0.3363 (17) | 0.2549 (16) | 0.7996 (15) | 0.068* |
| H2W | 0.222 (3) | 0.2958 (17) | 0.7377 (9) | 0.068* |
| O2W | 0.02782 (18) | 0.31581 (13) | 0.27799 (11) | 0.0638 (4) |
| H3W | 0.094 (3) | 0.329 (2) | 0.3246 (12) | 0.096* |
| H4W | 0.039 (3) | 0.3485 (19) | 0.2309 (13) | 0.096* |

Atomic displacement parameters (Å²)

| | 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 | 0.0596 (11) | 0.0403 (9) | 0.0299 (8) | 0.0007 (8) | 0.0195 (8) | -0.0022 (7) |
| C9 | 0.0282 (7) | 0.0235 (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 | 0.0578 (8) | 0.0461 (7) | 0.0336 (6) | -0.0087 (6) | 0.0081 (5) | 0.0003 (5) |
| O3 | 0.0862 (10) | 0.0462 (8) | 0.0341 (7) | -0.0067 (7) | 0.0110 (6) | 0.0054 (6) |
| C12 | 0.0292 (8) | 0.0353 (8) | 0.0347 (8) | -0.0005 (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 | 0.0582 (8) | 0.0419 (7) | 0.0389 (7) | 0.0020 (6) | 0.0169 (6) | 0.0080 (5) |
| O2W | 0.0590 (9) | 0.0902 (12) | 0.0417 (8) | -0.0211 (8) | 0.0049 (6) | 0.0076 (8) |

Geometric parameters (Å, °)

| | | | |
|-------------------------------------|-------------|-------------------------|------------|
| Cu—N2 | 2.0016 (12) | C5—H5B | 0.9700 |
| Cu—N2 ⁱ | 2.0016 (12) | C6—H6A | 0.9600 |
| Cu—N1 | 2.1086 (11) | C6—H6B | 0.9600 |
| Cu—N1 ⁱ | 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 ⁱ | 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 ⁱ | 180.0 | N2 ⁱ —C5—H5B | 109.9 |
| N2—Cu—N1 | 93.88 (5) | C4—C5—H5B | 109.9 |
| N2 ⁱ —Cu—N1 | 86.12 (5) | H5A—C5—H5B | 108.3 |
| N2—Cu—N1 ⁱ | 86.12 (5) | C1—C6—H6A | 109.5 |
| N2 ⁱ —Cu—N1 ⁱ | 93.88 (5) | C1—C6—H6B | 109.5 |
| N1—Cu—N1 ⁱ | 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 ⁱ —N2—C3 | 112.86 (11) | C3—C7—H7C | 109.5 |
| C5 ⁱ —N2—Cu | 109.37 (9) | H7A—C7—H7C | 109.5 |
| C3—N2—Cu | 119.42 (9) | H7B—C7—H7C | 109.5 |
| C5 ⁱ —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 ⁱ —C5—C4 | 108.89 (12) | H1W—O1W—H2W | 109.8 (15) |
| N2 ⁱ —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—N2 ⁱ | -54.16 (16) |
| C6—C1—C2—C3 | -160.03 (14) | C4—N1—C9—C10 | -40.36 (17) |
| C5 ⁱ —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 ⁱ —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 ⁱ —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, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N2—H1N \cdots O2 ⁱ | 0.87 (1) | 2.00 (1) | 2.8634 (18) | 173 (2) |
| N3—H2N \cdots O1W ⁱⁱ | 0.85 (2) | 2.19 (2) | 3.031 (2) | 170 (2) |
| N3—H3N \cdots O1 ⁱⁱⁱ | 0.86 (2) | 2.37 (2) | 3.221 (2) | 175 (1) |
| O1W—H2W \cdots O2 | 0.83 (1) | 1.94 (1) | 2.7574 (18) | 167 (2) |
| O1W—H1W \cdots O2W ^{iv} | 0.83 (2) | 1.98 (2) | 2.794 (2) | 167 (2) |
| O2W—H3W \cdots O3 | 0.83 (2) | 1.96 (2) | 2.779 (2) | 169 (2) |
| O2W—H4W \cdots O1 ^v | 0.82 (2) | 2.06 (2) | 2.869 (2) | 168 (2) |

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