



# [*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

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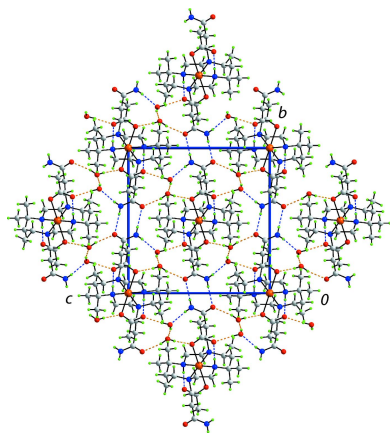
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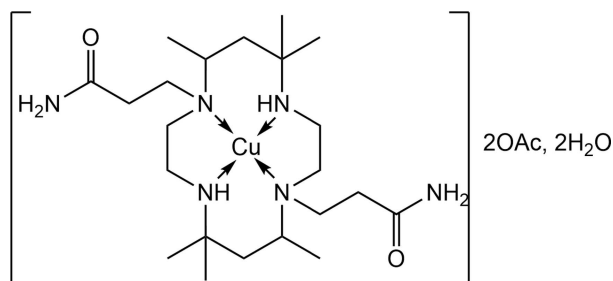
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The title Cu<sup>II</sup> macrocyclic complex salt tetrahydrate, [Cu(C<sub>22</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>)](C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, sees the metal atom located on a centre of inversion and coordinated within a 4 + 2 (N<sub>4</sub>O<sub>2</sub>) 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}<sub>2</sub> 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

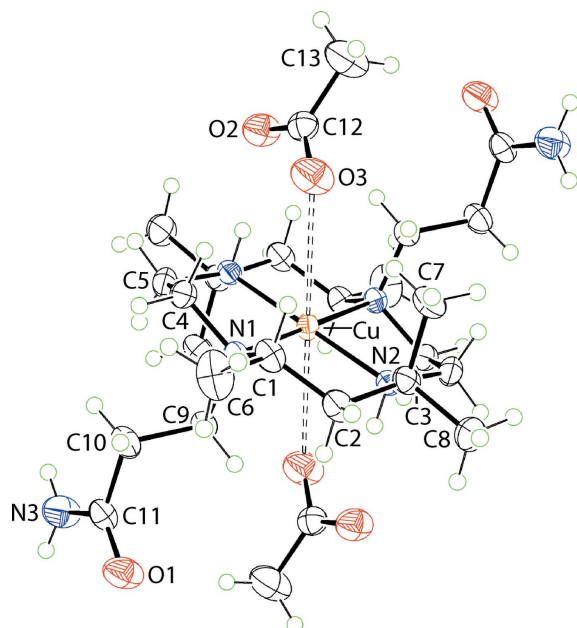
Owing to the multifarious applications of different metal complexes of a wide variety of macrocyclic ligands (Ali *et al.*, 2019; Bernhardt & Sharpe, 2000; Lamani *et al.*, 2018; Vicente *et al.*, 2003; Xu *et al.*, 2020), studies on some *N*-pendent macrocyclic ligands and their metal complexes were 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', C<sub>22</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>, 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)](O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 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 N<sub>4</sub>O<sub>2</sub> 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 CuN<sub>4</sub> plane are shown as dashed lines.

**Table 1**  
Hydrogen-bond geometry (Å, °).

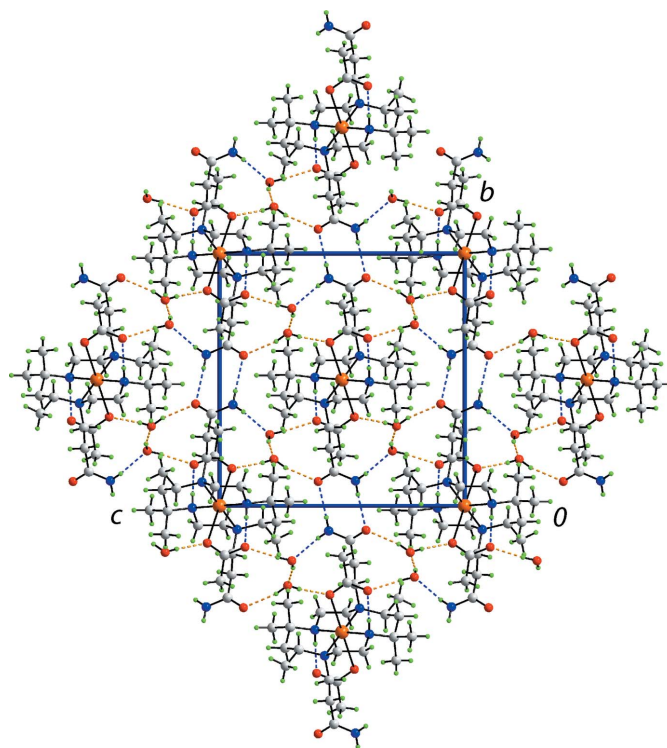
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N2–H1N···O2 <sup>i</sup>	0.87 (1)	2.00 (1)	2.8634 (18)	173 (2)
N3–H2N···O1W <sup>ii</sup>	0.85 (2)	2.19 (2)	3.031 (2)	170 (2)
N3–H3N···O1 <sup>iii</sup>	0.86 (2)	2.37 (2)	3.221 (2)	175 (1)
O1W–H2W···O2	0.83 (1)	1.94 (1)	2.7574 (18)	167 (2)
O1W–H1W···O2W <sup>iv</sup>	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 <sup>v</sup>	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 CuN<sub>4</sub> 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<sub>2</sub>}<sub>2</sub> 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)<sup>a</sup>.

Contact	Distance	Symmetry operation
O1W—H1W...O2W <sup>b</sup>	1.83	$x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$
O1W—H2W...O2 <sup>b</sup>	1.79	$x, y, z$
N3—H2N...O1W <sup>b</sup>	2.03	$-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$
O2W—H3W...O3 <sup>b</sup>	1.81	$x, y, z$
O2W—H4W...O1 <sup>b</sup>	1.90	$-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$
N2—H1N...O2 <sup>b</sup>	1.86	$-x + 1, -y + 1, -z + 1$
N3—H3N...O1 <sup>b</sup>	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

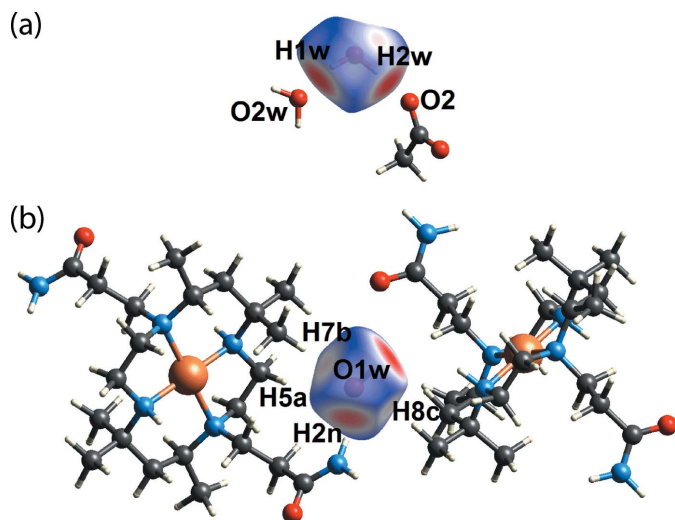


Figure 3

Two views of the Hirshfeld surface for the O1W-water molecule of (I) over  $d_{\text{norm}}$  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.

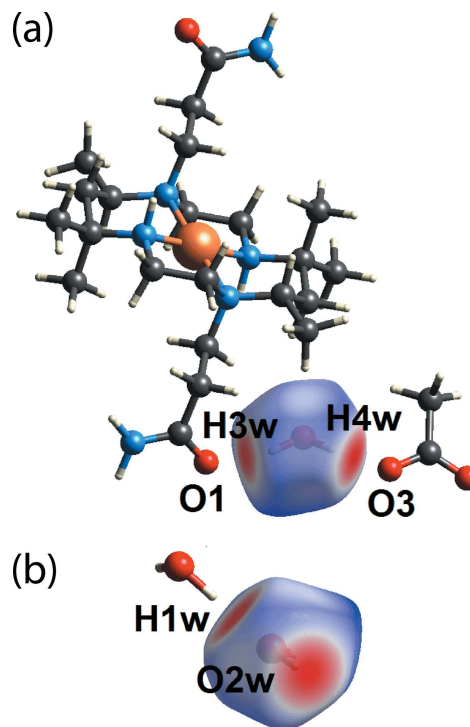


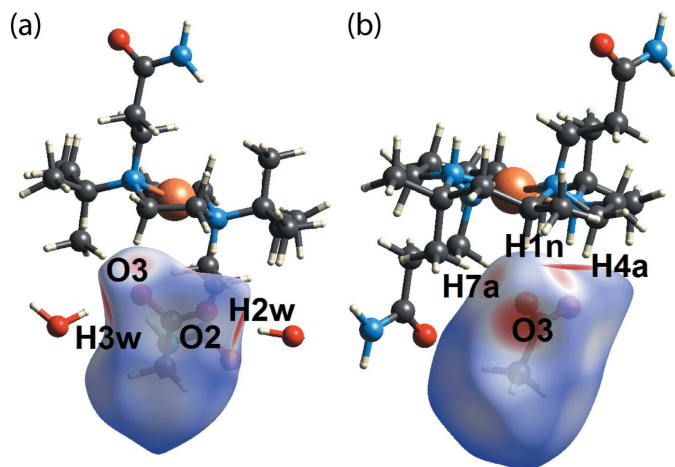
Figure 4

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

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.

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(carboxylate) 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(carboxylate) and water-O—H...O(water) 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(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)



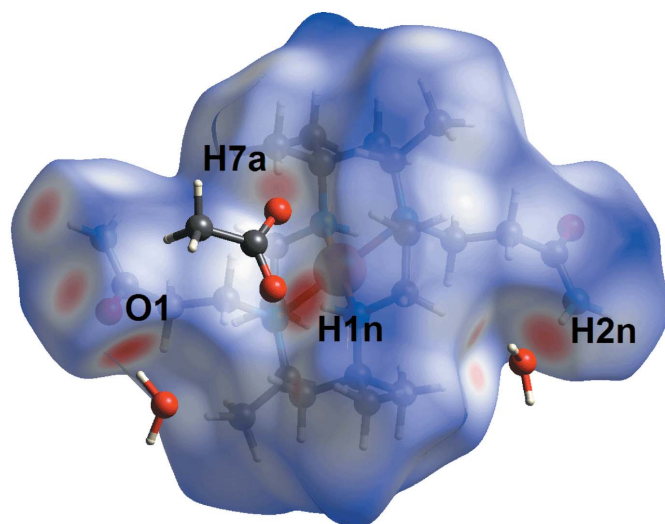
**Figure 5**  
Two views of the Hirshfeld surface for the anion in (I) over  $d_{\text{norm}}$  highlighting (a) conventional hydrogen bonds and (b) C–H $\cdots$ O interactions.

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  $d_{\text{norm}}$ -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 $\cdots$ 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  $d_{\text{norm}}$ -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



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

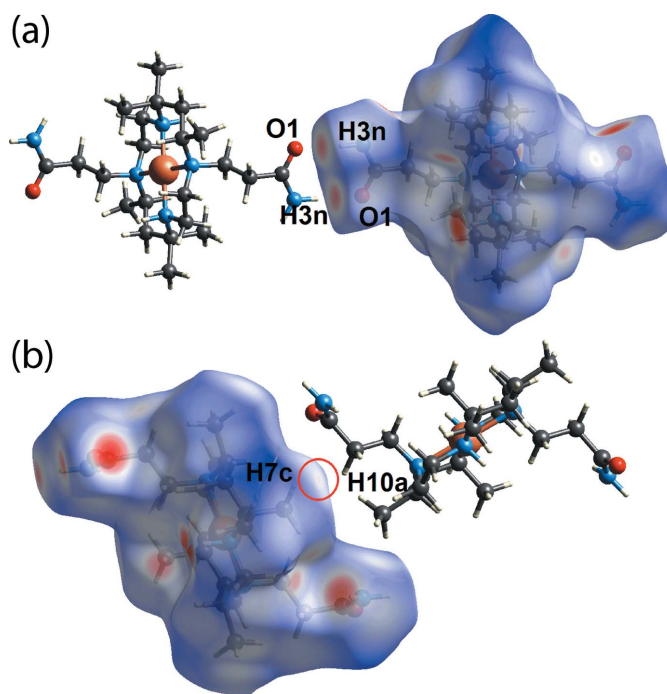
**Table 3**

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  $d_{\text{norm}}$  highlighting (a) amide-N–H $\cdots$ O(amide) hydrogen bonds and (b) H $\cdots$ H interactions.

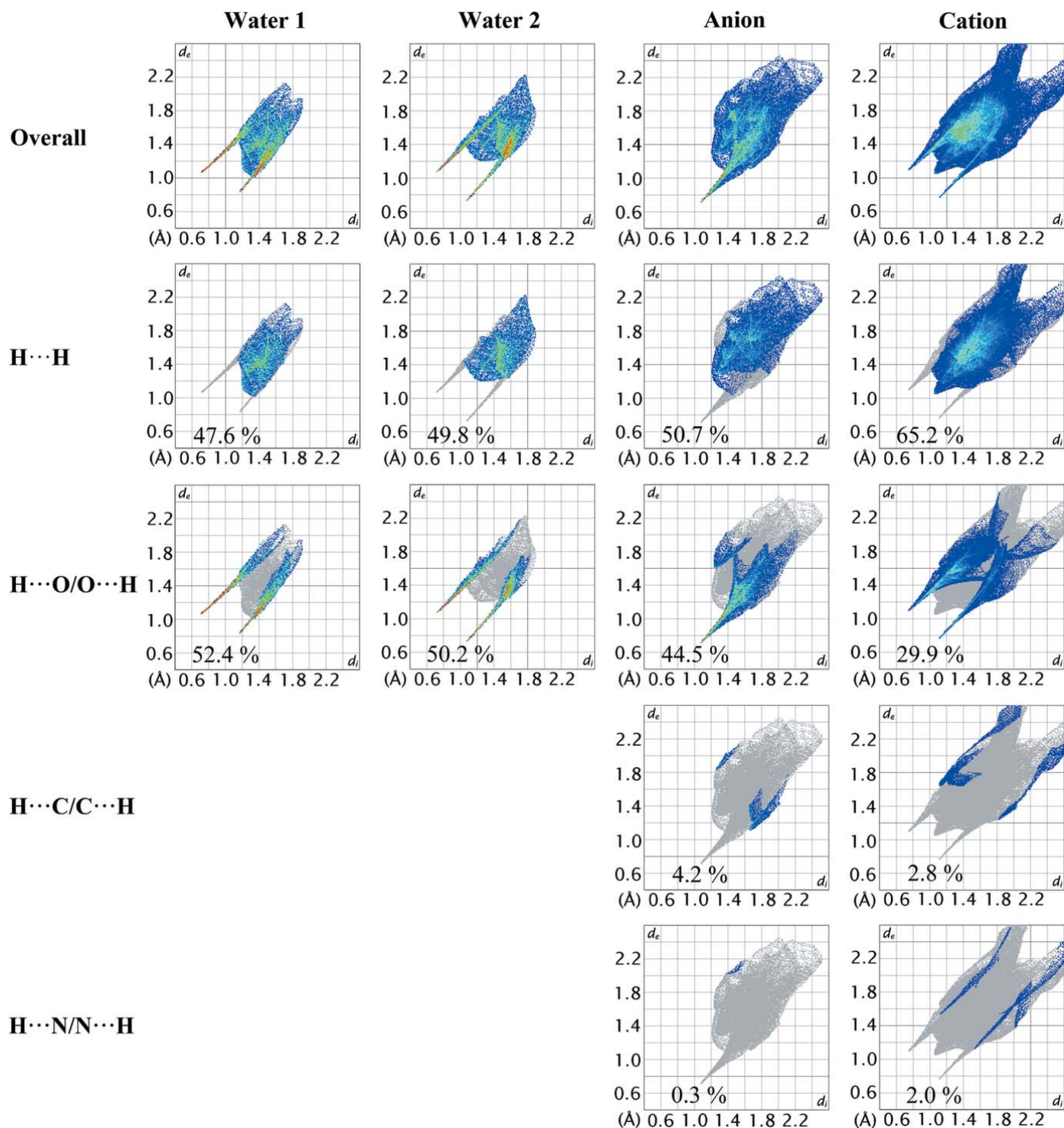


Figure 8

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<sup>II</sup> 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<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub> 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<sup>II</sup> 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)](O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (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 <sub>22</sub> H <sub>46</sub> N <sub>6</sub> O <sub>2</sub> )](C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
<i>M<sub>r</sub></i>	680.34
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <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)
$\beta$ (°)	97.525 (1)
<i>V</i> (Å <sup>3</sup> )	1695.24 (3)
<i>Z</i>	2
Radiation type	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	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> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.759, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	21762, 3022, 2902
<i>R</i> <sub>int</sub>	0.021
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.597
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>	0.029, 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 <sup>-3</sup> )	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*<sub>iso</sub>(H) set to 1.2–1.5*U*<sub>eq</sub>(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*<sub>iso</sub>(H) set to 1.5*U*<sub>eq</sub>(O) and 1.2*U*<sub>eq</sub>(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(C<sub>22</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>)](C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O  
*M<sub>r</sub>* = 680.34  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 8.5733 (1) Å  
*b* = 14.2616 (2) Å  
*c* = 13.9853 (1) Å  
 $\beta$  = 97.525 (1)°  
*V* = 1695.24 (3) Å<sup>3</sup>  
*Z* = 2

*F*(000) = 734  
*D<sub>x</sub>* = 1.333 Mg m<sup>-3</sup>  
 Cu *K*α radiation, λ = 1.54184 Å  
 Cell parameters from 15564 reflections  
 $\theta$  = 4.5–76.7°  
 $\mu$  = 1.41 mm<sup>-1</sup>  
*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<sup>-1</sup>  
 $\omega$  scans  
 Absorption correction: gaussian  
 (*CrysAlis PRO*; Rigaku OD, 2018)  
*T<sub>min</sub>* = 0.759, *T<sub>max</sub>* = 1.000  
 21762 measured reflections

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

*Refinement*

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.029  
*wR*(*F*<sup>2</sup>) = 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 ( $\text{\AA}^2$ )*

	<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 (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 <sup>i</sup>	2.0016 (12)	C6—H6A	0.9600
Cu—N1	2.1086 (11)	C6—H6B	0.9600
Cu—N1 <sup>i</sup>	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 <sup>i</sup>	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 <sup>i</sup>	180.0	N2 <sup>i</sup> —C5—H5B	109.9
N2—Cu—N1	93.88 (5)	C4—C5—H5B	109.9
N2 <sup>i</sup> —Cu—N1	86.12 (5)	H5A—C5—H5B	108.3
N2—Cu—N1 <sup>i</sup>	86.12 (5)	C1—C6—H6A	109.5
N2 <sup>i</sup> —Cu—N1 <sup>i</sup>	93.88 (5)	C1—C6—H6B	109.5
N1—Cu—N1 <sup>i</sup>	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 <sup>i</sup> —N2—C3	112.86 (11)	C3—C7—H7C	109.5
C5 <sup>i</sup> —N2—Cu	109.37 (9)	H7A—C7—H7C	109.5
C3—N2—Cu	119.42 (9)	H7B—C7—H7C	109.5
C5 <sup>i</sup> —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 <sup>i</sup> —C5—C4	108.89 (12)	H1W—O1W—H2W	109.8 (15)
N2 <sup>i</sup> —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 <sup>i</sup>	-54.16 (16)
C6—C1—C2—C3	-160.03 (14)	C4—N1—C9—C10	-40.36 (17)
C5 <sup>i</sup> —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 <sup>i</sup> —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 <sup>i</sup> —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 <sup>i</sup>	0.87 (1)	2.00 (1)	2.8634 (18)	173 (2)
N3—H2N $\cdots$ O1W <sup>ii</sup>	0.85 (2)	2.19 (2)	3.031 (2)	170 (2)
N3—H3N $\cdots$ O1 <sup>iii</sup>	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 <sup>iv</sup>	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 <sup>v</sup>	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)  $-x+1/2, y-1/2, -z+1/2$ .