

Crystal structure and Hirshfeld surface analysis of $(\mu\text{-}2\text{-}\{4\text{-}[(\text{carboxylatomethyl})\text{carbamoyl}]\text{benz-amido}\}\text{acetato-}\kappa^2\text{O:O}')\text{bis}[\text{bis}(1,10\text{-phenanthroline-}\kappa^2\text{N,N}')\text{copper(II)}]\text{dinitrate } N,N'\text{-}(1,4\text{-phenyl-enedicarboxyl})\text{diglycine monosolvate octahydrate}$

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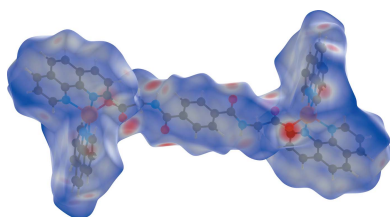
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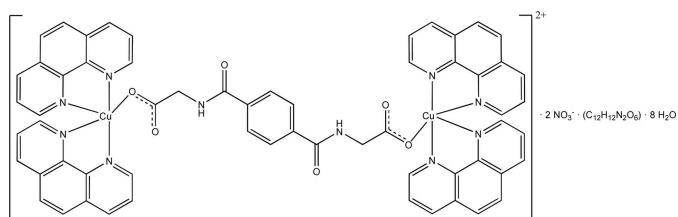
The centrosymmetric binuclear complex cation of the title compound, $[\text{Cu}_2(\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_6)(\text{C}_{12}\text{H}_8\text{N}_2)_4](\text{NO}_3)_2 \cdot \text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_6 \cdot 8\text{H}_2\text{O}$, is composed of a Cu^{II} atom with a distorted trigonal-bipyramidal coordination environment defined by four N atoms from two bidentate 1,10-phenanthroline ligands and one oxygen atom from one-half of the monodentate N,N' -(1,4-phenylenedicarbonyl)diglycinate anion. The asymmetric unit is completed by one-half of the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule, which is located on a centre of inversion, by one nitrate counter-anion and four water molecules. In the crystal, the cationic complexes are linked *via* intermolecular $\pi\text{-}\pi$ stacking and through lone-pair $\cdots\pi$ interactions involving the N,N' -(1,4-phenylenedicarbonyl)diglycinate anion and the phenanthroline ligands. The N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule is involved in classical and non-classical hydrogen-bonding interactions, as well as $\pi\text{-}\pi$ stacking interactions. The centroid-to-centroid distances between aromatic entities are in the range 3.5402 (5)–4.3673 (4) Å. The crystal structure is stabilized by further C–H \cdots O contacts as well as by O–H \cdots O and N–H \cdots O hydrogen bonds between water molecules, the nitrate anions, the N,N' -(1,4-phenylenedicarbonyl)diglycinate ligands, N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecules and phenanthroline ligands, giving rise to a supramolecular framework. A Hirshfeld surface analysis was carried out to quantify these interactions.

1. Chemical context

Over the past two decades, the syntheses and structural investigations of coordination polymers with different dimensions as well as metal–organic frameworks (MOFs) have attracted much attention because of their intriguing functional architectures and applications (Batten *et al.*, 2013; Leong & Vittal, 2011; Yamada *et al.*, 2013). Potential applications of these materials are in catalysis, gas storage (Kitagawa *et al.*, 2004), luminescence (Allendorf *et al.*, 2015) or as scintillators (Allendorf *et al.*, 2009; Doty *et al.*, 2009; Perry *et al.*, 2012). Their crystal structures show various non-covalent intermolecular interactions and forces, and therefore are highly connected to their supramolecular chemistry (Schneider, 2009) and self-assembly (Cook *et al.*, 2013). Moreover, these compounds have a high relevance in biological systems interacting with macromolecules such as DNA, RNA or



proteins (Salonen *et al.*, 2011), and also in biochemical reactions as protein–ligand recognitions or in drug-delivery systems of biologically active agents (Meyer *et al.*, 2003). In general, for all these supramolecular interactions, weaker and reversible intermolecular forces play the key role, including metal coordination, classical and non-classical hydrogen bonding of the types O–H···O, N–H···O and C–H···O, respectively, different π -interactions involving the aromatic rings such as π – π stacking, C–H··· π , ion··· π and lone-pair··· π interactions. Metal-coordinating and nitrogen-containing heterocycles such as bipyridines and phenanthrolines are electron-deficient aromatic ring systems and thus predestined to be acceptors in π – π stacking, ion··· π or lone-pair··· π interactions (Janiak, 2000; Berryman & Johnson, 2009). In addition, π -donor···acceptor functions in different parts of an aromatic molecule can lead to remarkable properties (Albrecht *et al.*, 2010). Transition-metal coordination compounds with the pseudo aromatic diamino acid *N,N'*-(1,4-phenylenedicarbonyl)diglycine, forming zigzag chains and constructing interpenetrating networks, have been described in the literature (see *Database survey*).



In our synthetic approach, we employ such systems as electron-deficient bidentate aromatic ring systems such as phenanthroline or bipyridine in order to block parts of the metal cation coordination sphere. Thus, the alternative assembly process lies in the use of the offered different π -interaction possibilities, *viz.* π – π stacking, C–H··· π , ion··· π and lone-pair··· π and not in forming the aforementioned zigzag chains. We have previously reported structural studies of two cobalt complexes with bidentate bipyridine or bidentate phenanthroline ligands and a non-coordinating *N,N'*-(1,4-phenylenedicarbonyl)diglycine molecule in the crystal (Pook *et al.*, 2014, 2015). In these structures, the *N,N'*-(1,4-phenylenedicarbonyl)diglycine molecule is deprotonated and thus acts as counter-anion. In the two structures, the embedded *N,N'*-(1,4-phenylenedicarbonyl)diglycinate molecule links the cationic building blocks by numerous supramolecular interactions.

In a continuation of this work, we have now synthesized and determined the structure of a novel copper(II) coordination compound where the *N,N'*-(1,4-phenylenedicarbonyl)diglycine moiety is a bis-monodentate bridging anionic ligand in its deprotonated form, as well as a solvent molecule in its neutral form in one crystal structure. The structural investigation and description of the supramolecular network is confirmed and discussed with the aid of a Hirshfeld surface analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) of the cationic complex and the *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent molecule.

2. Structural commentary

The binuclear and centrosymmetric complex cation of the title compound, $[\text{Cu}_2(\text{C}_{12}\text{H}_8\text{N}_2)_4(\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_6)](\text{NO}_3)_2 \cdot (\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_6) \cdot 8\text{H}_2\text{O}$, comprises two bidentate phenanthroline ligands and one bridging monodentate *N,N'*-(1,4-phenylenedicarbonyl)diglycinate ligand for each Cu^{II} atom, defining a distorted trigonal–bipyramidal coordination sphere. A crystallographic centre of inversion is located at the centroid of the bridging *N,N'*-(1,4-phenylenedicarbonyl)diglycinate anion as well as the neutral and non-coordinating *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent molecule. The asymmetric unit is completed by one non-coordinating nitrate counter-anion and four water molecules (Fig. 1).

The equatorial plane of the Cu^{II} coordination environment is occupied by O1, N2 and N4 atoms with bond lengths of 2.235 (5), 2.119 (2) and 2.111 (3) Å, and the axial positions by N1 and N3 with shorter bonds each of 1.974 (3) Å, respectively. The bond angle N1–Cu–N3 is 174.71 (11)°. The sum of the bond angles O1–Cu–N2 [136.69 (11)°], O1–Cu–N4 [103.88 (12)°] and N2–Cu–N4 [118.90 (10)°] in the equatorial plane amounts to 359.47°, indicating only slight distortions. Distances and angles within the distorted trigonal–bipyramidal coordination sphere of the Cu^{II} ion are similar to those found in the literature (Santha Lakshmi & Samundeeswari, 2015; Lim *et al.* 2014). The nearly identical bond lengths of the carboxylate group in the bridging ligand [C30–O1 = 1.249 (5) and C30–O2 = 1.249 (6) Å] indicate a delocalized bonding arrangement, rather than localized single and double bonds as in the case of the carboxylic group of the neutral *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent molecule [C36–O4 = 1.205 (6) and C36–O5 = 1.316 (5) Å]. The O1–C30–O2 angle of 123.1 (4)° in the carboxylate group is slightly smaller than in the carboxylic group [O4–C36–O5 = 124.3 (4)°]. In the coordinating *N,N'*-(1,4-phenylenedicarbonyl)diglycinate ligand, the deviations of atoms defining the central benzamido entity from its least-squares plane are 0.040 (4) Å (C28), –0.084 (3) Å (O3), 0.245 (4) Å

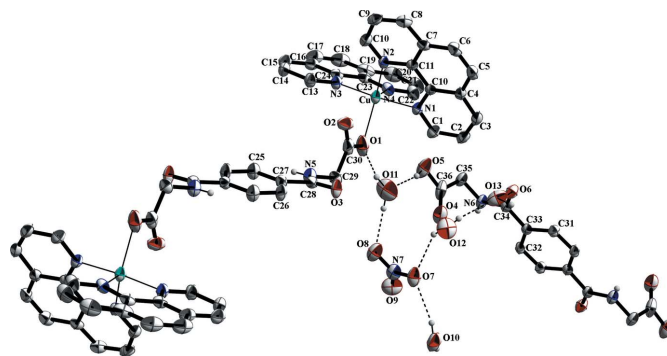


Figure 1

The structures of molecular entities in the title compound with atom labels and displacement ellipsoids of non-H atoms at the 40% probability level. Dashed lines indicate O–H···O hydrogen bonds (see Table 1 for details). Unlabelled atoms are related to labelled ones by the symmetry operation $-x, -y, -z + 1$ for the cationic complex and $-x, -y + 2, -z + 2$ for the *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent molecule.

(N5) and 0.404 (4) Å (C29), while in the *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent they are -0.018 (4) Å (C34), 0.102 (3) Å (O6), -0.192 (4) Å (N6) and -0.257 (4) Å (C35). The angle between the amide group and the carboxylate group connected through the sp^3 -hybridized methylene carbon atom (N5–C29–C30) is 113.6 (3)°, and for the neutral solvent molecule it is (N6–C35–C36) 112.1 (3)°. The dihedral angle between the planar carboxylate group (O1/C30/O2) and the aromatic synthon (C25–27/C25'–C27') of the ligand is 84.1 (3)° and thus smaller than the value found in the free solvent molecule of the aromatic synthon (C31–C33/C31'–C33') and the planar carboxylate group (O4/C36/O5) at 88.9 (3)°. The dihedral angle between the mean planes of the two bidentate phenanthroline ligands is 61.71 (5)°; the corresponding value between phenanthroline (N1/C1–C12/N2) and the coordinating carboxylate group (O1/C30/O2) is 79.9 (4)° and between phenanthroline (N3/C13–C24/N4) and the carboxylate group is 82.5 (3)°, respectively.

3. Supramolecular features

In the crystal structure, numerous non-covalent interactions are observed. The nitrate anions are linked *via* O–H···O, C–H···O and partly *via* N–H···O hydrogen bonds with

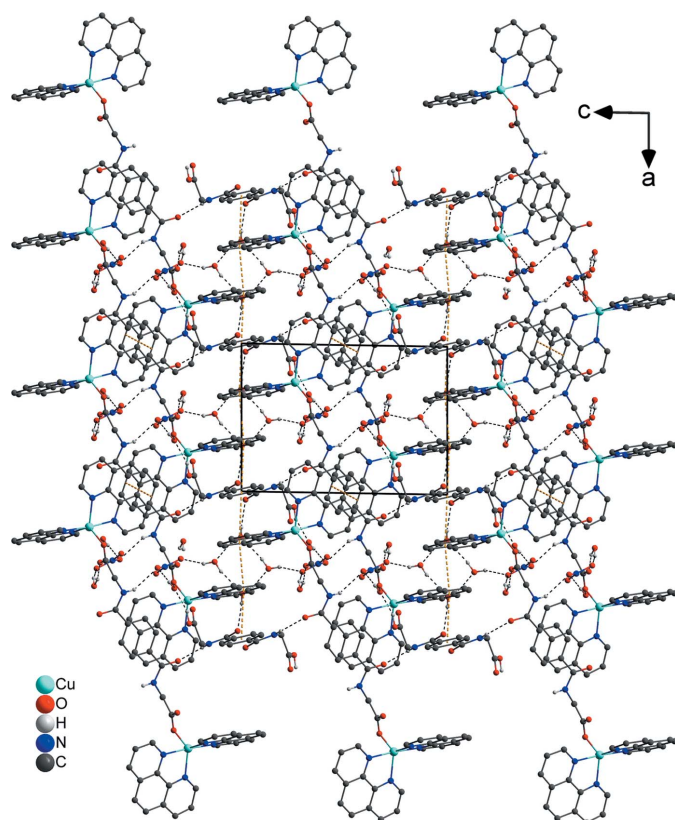


Figure 2

The crystal packing of the title structure in a view along the *b* axis. Selected π – π stacking interactions between phenanthroline ligands and *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent and phenanthroline ligands are shown as orange dashed lines as well as classical hydrogen bonding indicated by black dashed lines. The hydrogen atoms of aromatic moieties and methylene groups have been omitted for clarity.

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>
O5–H5···O11	0.87 (6)	1.84 (6)	2.665 (5)	159 (6)
O10–H10A···O2 ⁱ	0.83 (7)	2.06 (7)	2.878 (6)	168 (7)
O10–H10B···O7	0.85 (7)	2.24 (7)	3.033 (6)	155 (7)
O11–H11A···O8	0.85	2.00	2.848 (6)	179
O11–H11B···O1	1.00	1.68	2.643 (6)	160
O12–H12A···O7	0.79 (8)	2.32 (8)	3.024 (6)	149 (8)
O12–H12B···O13	0.80 (8)	2.07 (8)	2.856 (6)	170 (8)
O13–H13A···O12 ⁱⁱ	0.75 (7)	2.05 (7)	2.757 (6)	157 (8)
O13–H13B···O6	0.81 (7)	2.05 (7)	2.851 (4)	170 (7)
N5–H5N···O8 ⁱⁱⁱ	0.79 (4)	2.23 (5)	2.947 (4)	152 (4)
N6–H6···O3 ^{iv}	0.75 (4)	2.26 (4)	2.995 (4)	167 (4)
C2–H2···O13	0.94	2.37	3.302 (5)	172
C3–H3···O10 ⁱⁱ	0.94	2.44	3.358 (7)	165
C9–H9···O4 ^v	0.94	2.40	3.099 (5)	131
C13–H13···O2	0.94	2.42	3.031 (5)	122
C14–H14···O10 ⁱⁱⁱ	0.94	2.60	3.414 (5)	145
C25–H25···O9 ⁱⁱⁱ	0.94	2.53	3.354 (6)	147
C32–H32···O3 ^{iv}	0.94	2.48	3.388 (4)	163
C35–H35A···O10 ^{vi}	0.98	2.53	3.378 (5)	145

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

water solvent molecules, the phenanthroline ligands and the metal-coordinating *N,N'*-(1,4-phenylenedicarbonyl)diglycinate ligands (Figs. 1–3; Table 1). π – π interactions between parallel-displaced phenanthroline ligands and between phenanthroline and the free *N,N'*-(1,4-phenylenedicarbonyl)diglycine solvent molecule, as well as between phenanthroline ligands and the metal-coordinating *N,N'*-(1,4-phenylenedicarbonyl)diglycinate ligand stack these components along the different axes (Figs. 2–4). Centroid-to-centroid

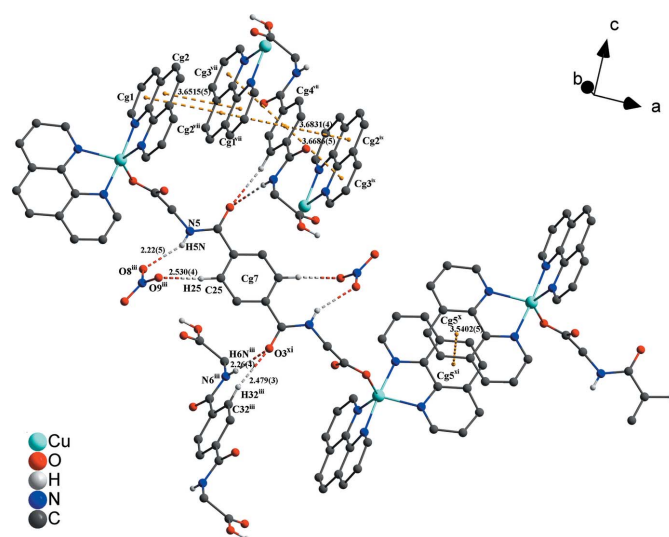


Figure 3

In the crystal packing, different non-covalent interactions such as C–H···O and N–H···O contacts and π – π stacking interactions between the aromatic moieties are present. C–H···O and N–H···O interactions are indicated by red–white dashed lines and π – π stacking by dark-yellow dashed lines. The hydrogen atoms not involved in interactions have been omitted for clarity. Distances are given in Å. [Symmetry codes: (iii) $-x + 1, -y + 1, -z + 1$; (vii) $-x + 1, -y, -z + 2$; (viii) $x + 1, y - 1, z$; (ix) $x + 1, y, z$; (x) $x + 2, y - 1, z$; (xi) $-x + 2, -y, -z + 1$.]

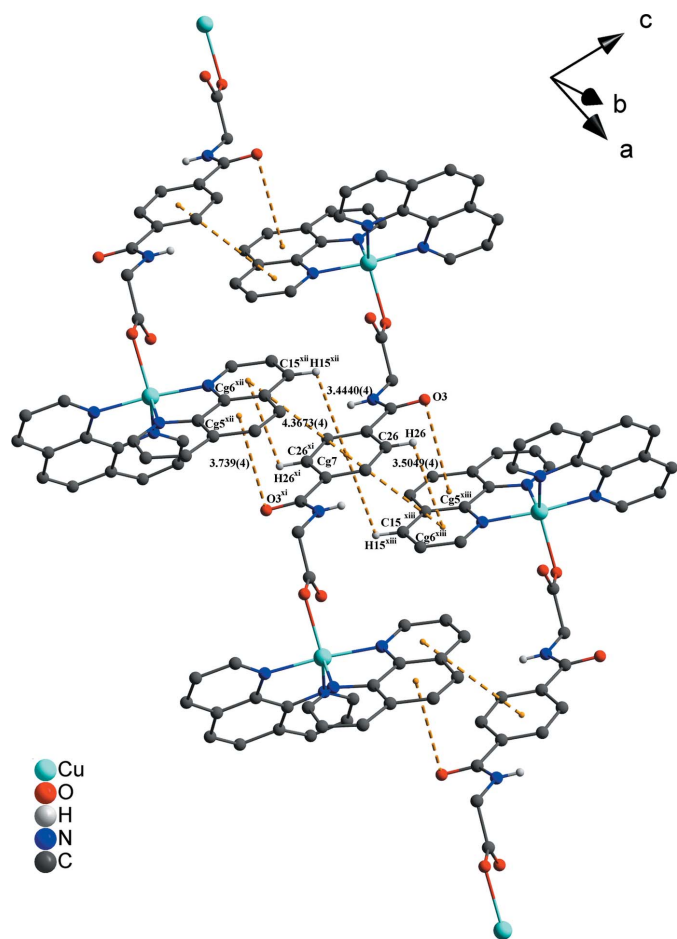


Figure 4
View of the lone-pair $\cdots\pi$ interaction and π - π stacking between the complex cation subunits. Non-covalent interactions are indicated by dark-yellow dashed lines. The hydrogen atoms not involved in interactions have been omitted for clarity. Distances are given in Å. [Symmetry codes: (xii) $-x + 1, -y, -z + 1$; (xiii) $x + 1, y, z$.]

distances are: 3.6515 (5) Å between $Cg1\cdots Cg2$, 3.6831 (4) Å between $Cg2\cdots Cg4$, 3.6686 (5) Å between $Cg3\cdots Cg4$, and 3.5402 (5) Å between $Cg5\cdots Cg5$, where $Cg1$, $Cg2$, $Cg3$, $Cg4$ and $Cg5$ are the centroids defined by the ring atoms N1/C1–C4/C12, C4–C7/C11–C12, N2/C7–C11, C31–C33/C31'–C33' and C16–C19/C23–C24, respectively. These distances are in expected ranges (Barceló-Oliver *et al.*, 2010; Kumar Seth *et al.*, 2010). In addition, another offset face-to-face arrangement between a phenanthroline and the metal-coordinating N,N' -(1,4-phenylenedicarbonyl)diglycinate ligand leads to a longer $Cg6\cdots Cg7$ separation of 4.3673 (4) Å (Fig. 4), where $Cg6$ and $Cg7$ are the centroids defined by the ring atoms N3/C13–C16/C24 and C25–C27/C25'–C27', respectively. Such weaker π -stacking interactions have been discussed in the past as being relevant (Avasthi *et al.*, 2014; Dance, 2003; Janiak, 2000; Martinez & Iverson, 2012; Piovesan *et al.*, 2016; Salonen *et al.*, 2011). The dihedral angle between the mean planes of the mentioned aromatic rings is 3.50 (12)°. The angle between the lines through C15/ $Cg7$ and the centroids through $Cg6/Cg7$ is 17.05 (7)° and is slightly increased in comparison with the lines

through C26/ $Cg7$ and the centroids $Cg6/Cg7$ with a value of 16.99 (5)°. Distances shown in Fig. 4 between atoms and centroids of H15/ $Cg7$ and C15/ $Cg7$ are 3.4440 (4) and 3.676 (6) Å and between H26/ $Cg7$ and C26/ $Cg7$ are 3.5049 (4) and 3.713 (5) Å with observed angles of 96.8 (3)° (C15–H15 $\cdots Cg7$) and 95.4 (3)° (C16–H26 $\cdots Cg7$), respectively. Besides the previously mentioned forces, a lone-pair $\cdots\pi$ interaction between the O3 atom of the carboxylate group of the metal-coordinating N,N' -(1,4-phenylenedicarbonyl)diglycinate ligand and the $Cg5$ centroid of a phenanthroline ligand are observed and associated with a distance of 3.739 (4) Å. This value is similar to those found in the literature (Egli & Sarkhel, 2007; Gao *et al.*, 2009; Mooibroek *et al.*, 2008; Wan *et al.*, 2008). Finally, π -interactions between $Cg5$ and $Cg7$ and the adjacent lone-pair $\cdots\pi$ interactions stack the cationic complex subunits along the a -axis direction and contribute to the consolidation of the supramolecular framework (Fig. 4).

4. Hirshfeld surface analysis

Substantiation and visualization of the described supramolecular features in the crystal structure and their close contacts between different molecular moieties, molecules, ionic and complex subunits can be achieved by using a Hirshfeld surface (HS) analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009). *Crystal Explorer* (Turner *et al.*, 2017, Wolff *et al.*, 2012) offers the possibility to investigate and explore the short atom-to-atom contacts to identify their potential for hydrogen-bonding and π -stacking interactions by generating the Hirshfeld surfaces mapped over d_{norm} , the electrostatic potential, the shape-index and the curvedness.

The HS mapped over d_{norm} of the cationic complex subunit in the range -0.7078 to 1.7629 a.u. and of the non-coordinating N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule in the range -0.6806 to 1.9484 a.u. are shown in Fig. 5 and Fig. 8, respectively. The corresponding quantitative contribution of intermolecular interactions are displayed in the overall two-dimensional fingerprint plots (FPs) and those

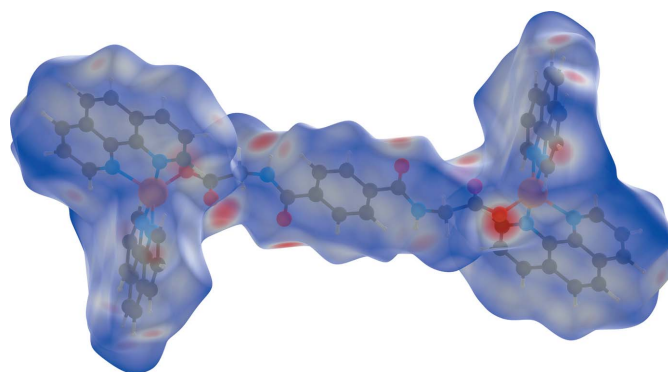


Figure 5
Graphical representation of the three-dimensional Hirshfeld surface (d_{norm}) for the cationic complex plotted in the range -0.7078 to 1.7629 a.u.. The surface is drawn with transparency and the surface regions with strongest intermolecular interactions are drawn in red.

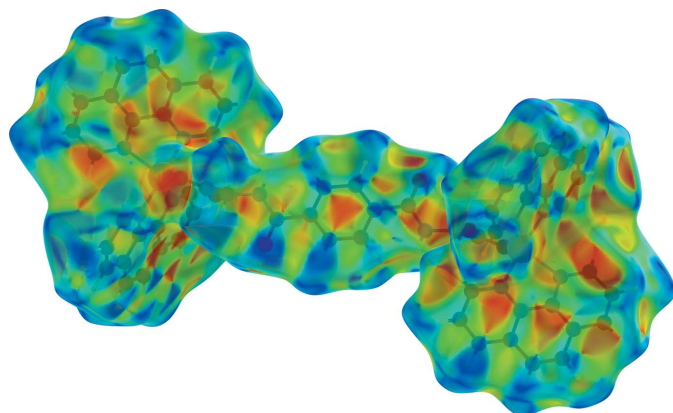


Figure 6
Hirshfeld surface drawn with transparency and mapped over the shape-index for the cationic complex. Red and blue triangles at the phenanthroline ligands and the N,N' -(1,4-phenylenedicarbonyl)diglycinate ligand indicate the regions involved in π - π stacking interactions.

split up into their descending order of crystal cohesion contributions in Fig. 7 and Fig. 11, respectively. The white areas of the HS indicate contacts with distances equal to the sum of van der Waals radii and the blue regions indicate longer distances than the van der Waals radii as depicted in Figs. 5 and 8. The bright-red spots as indicators of close contacts with shorter distances than the van der Waals radii represent the donor and acceptor functions of dominant classical and non-classical hydrogen-bonding interactions of the types $O-H\cdots O$, $N-H\cdots O$ and $C-H\cdots O$. This is confirmed by the appearance of large sharp asymmetrical spikes in the $H\cdots O/O\cdots H$ FPs (Figs. 7, 11) in the region of $d_e \sim 1.19 \text{ \AA}/d_i \sim 0.85 \text{ \AA}$ and $d_i \sim 0.68 \text{ \AA}/d_e \sim 1.02 \text{ \AA}$ as well as $d_e \sim 1.05 \text{ \AA}/d_i \sim 0.70 \text{ \AA}$ and $d_i \sim 1.12 \text{ \AA}/d_e \sim 0.78 \text{ \AA}$, which comprise 27.9% and 42.2% of the total amount on the HS, respectively.

In order to classify the donor and acceptor groups of the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule involved in hydrogen bonding, the HS mapped over the electrostatic potentials were calculated using *TONTO* (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005) with standard settings of the STP-3G basis set at Hartree-Fock theory. The appearance of blue and red surface regions indicates the positive and negative electrostatic potential as shown in Fig. 10, suggesting that the carbonyl oxygen atom of the amide group and the non-protonated oxygen atom of the carboxylate group act as hydrogen-bond acceptors whereas the nitrogen/hydrogen atoms of the amide group and the protonated oxygen atom of the carboxy group as well as the carbon/hydrogen atoms of the aromatic moiety act as hydrogen-bond donors. $H\cdots H$ contacts compromise 36.4% to the cationic complex as the largest contribution and 29.8% to the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule as the second largest contribution within the HS. This high relevance for the HS is attributed to the high proportion of hydrogen atoms in the structure of these entities. The $H\cdots N/N\cdots H$ contacts contribute 3.7% to the cationic complex and 3.4% to the solvent molecule to the total HS, respectively. Short

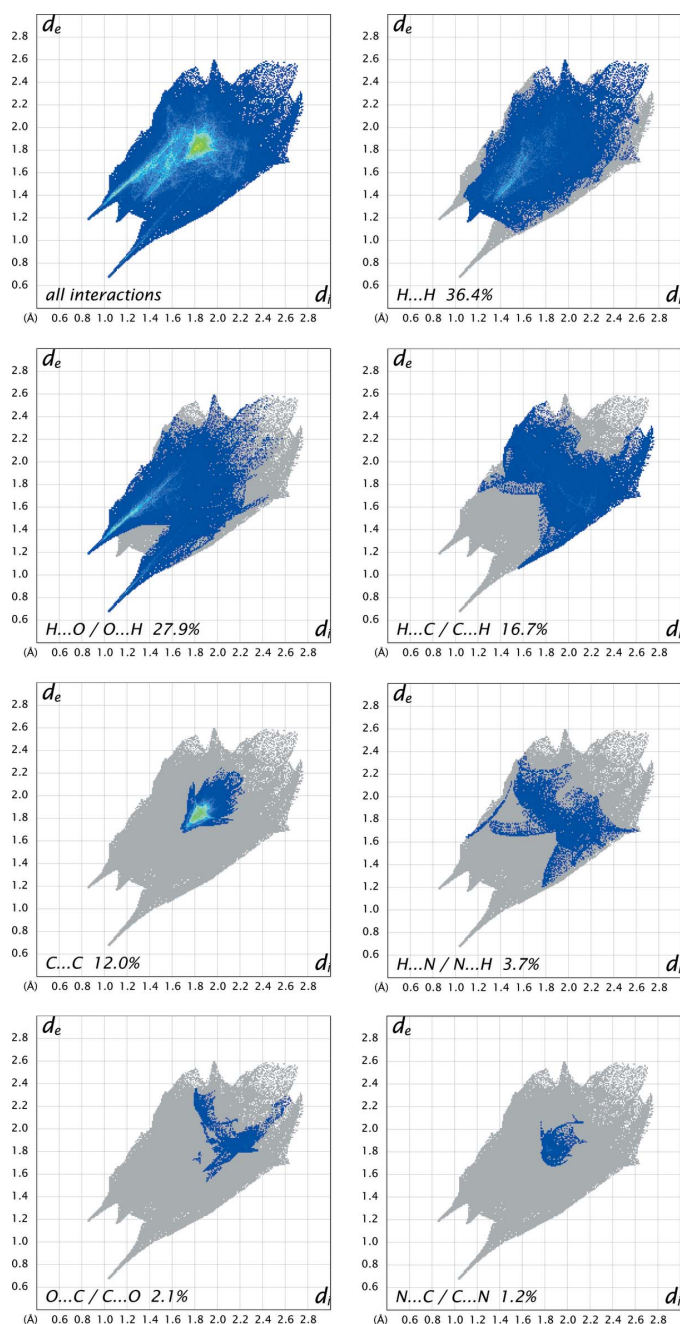


Figure 7
The full two-dimensional fingerprint plots for the cationic-complex subunit, showing all interactions and split up into contributions from different contacts. The d_i and d_e values are the closest internal and external distances (in \AA) from given points on the Hirshfeld surface contacts.

contacts of the solvent molecule with a minor contribution to the lattice of $O\cdots N/N\cdots O$ (0.4%) and $O\cdots O$ (0.1%) are also observed. The contribution of the different π - π interactions used for the stacking of the cationic complex subunits and the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule along the different axes is also significant for both entities. Therefore, the close $H\cdots C/C\cdots H$ (16.7%), $C\cdots C$ (12.0%), $O\cdots C/C\cdots O$ (2.1%) and $N\cdots C/C\cdots N$ (1.2%) contacts of the cationic complex are assigned to $C-H\cdots\pi$ interactions, π - π

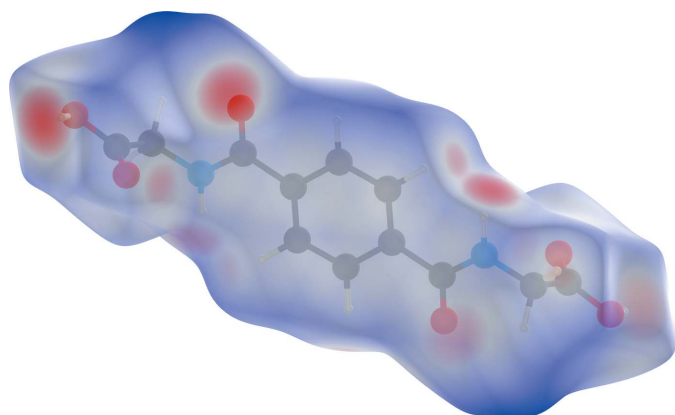


Figure 8
Hirshfeld surface for the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule with d_{norm} over the range -0.6806 to 1.9484 a.u.. The surface is drawn with transparency; red spots indicate the strongest intermolecular interactions.

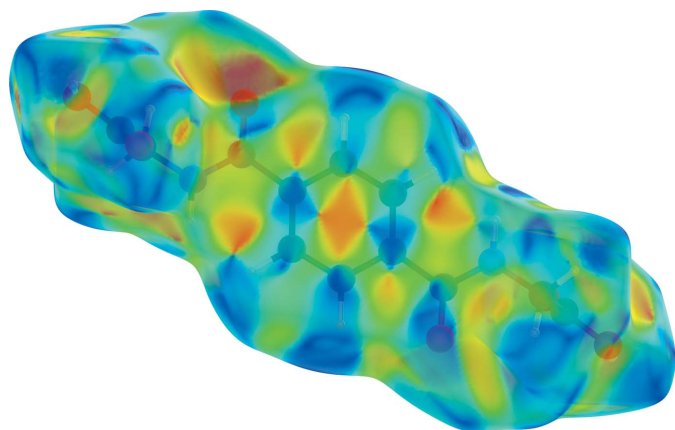


Figure 9
Hirshfeld surfaces drawn with transparency and mapped over the shape-index for the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule. Red and blue triangles indicate the region involved in π - π stacking interactions.

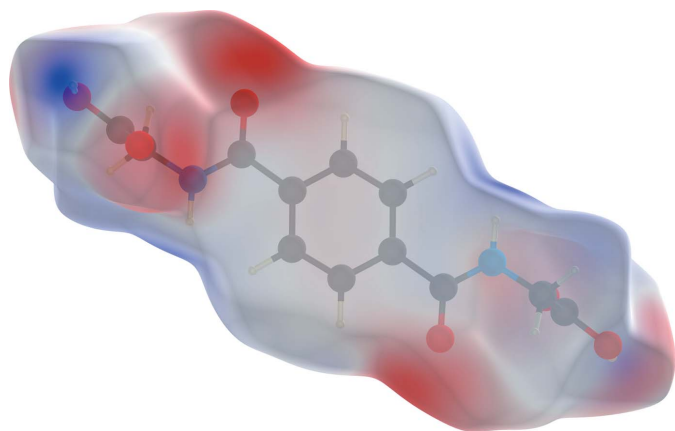


Figure 10
View of the transparent three-dimensional Hirshfeld surface of the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule plotted over electrostatic potential energy in the range -0.0828 to 0.1815 a.u. using the STO-3G basis set at the Hartree-Fock level. The $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bond donor and acceptor atoms are displayed as blue and red regions around the atoms corresponding to positive and negative potentials, respectively.

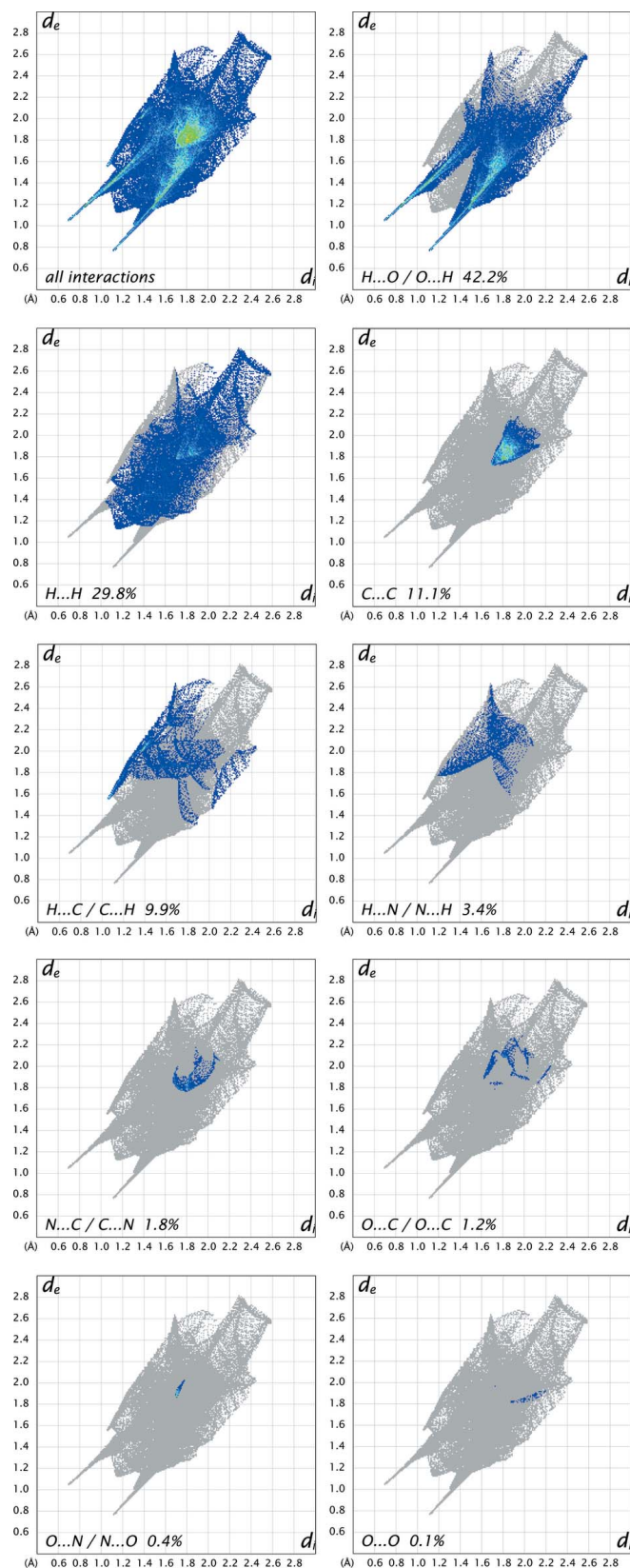


Figure 11
The full two-dimensional fingerprint plots for the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule, showing all interactions, and delineated into the contributions from different contacts. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

stacking (face-to-face) and lone-pair $\cdots\pi$ interactions of the carbonyl group and stacking between the phenanthroline ligands (Figs. 3, 4 and 7). For the N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule, the close C \cdots C (11.1%), H \cdots C/C \cdots H (9.9%), N \cdots C/C \cdots N (1.8%) and O \cdots C/C \cdots O (1.2%) contacts are assigned to π - π stacking (face-to-face), C-H $\cdots\pi$ interactions and stackings of the phenanthrolines and lone-pair $\cdots\pi$ interactions of the carbonyl group (Figs. 3, 4 and 11). This corresponds to the appearance of the red triangles of the aromatic moieties of the bidentate phenanthroline ligands, the metal-coordinating N,N' -(1,4-phenylenedicarbonyl)diglycinate ligand as well as the non-coordinating N,N' -(1,4-phenylenedicarbonyl)diglycine solvent molecule in the HS mapped over the shape-index, which represent the face-to-face π - π stacking interactions (Figs. 6, 9).

5. Database survey

A search for crystal structures containing the ligand N,N' -(1,4-phenylenedicarbonyl)diglycine using *SciFinder* (SciFinder, 2019) and the Cambridge Structural Database (Version 5.35, November 2013 with three updates; Groom *et al.*, 2016) resulted in six entries (Duan *et al.*, 2010; Kostakis *et al.*, 2005, 2011; Zhang *et al.*, 2005, 2006). Some of these structures are composed of interpenetrating networks as mentioned in the *Chemical context*. Among them are two structures which include bipyridine or phenanthroline ligands besides N,N' -(1,4-phenylenedicarbonyl)diglycine, and their structures show a number of non-classical interactions (Pook *et al.*, 2014, 2015).

6. Synthesis and crystallization

The starting material, N,N' -(1,4-phenylenedicarbonyl) diglycine, was prepared by the method of Cleaver & Pratt (1955). Cesium carbonate (2 mmol), 1,10-phenanthroline (1 mmol) and 2,2'-(benzene-1,4-dicarboxamido)diacetic acid (1 mmol) were dissolved in a 1:1 (v/v) mixture of water and methanol (50 ml) and refluxed for 30 minutes. The mixture was allowed to cool to room temperature, and a previously prepared aqueous solution of copper acetate (1 mmol) was slowly added under continuous stirring. Pale-blue block-shaped crystals of the title compound were obtained by slow evaporation at room temperature.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound H atoms were positioned with idealized geometry and refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C-H(aromatic) = 0.94 Å and C-H(methylene) = 0.98 Å using a riding model. The water H atoms were located in a difference-Fourier map and were refined with O-H distances restrained to 0.82–0.87 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, except O11–H11A with a fixed distance of 1.00 Å, which led to a stable and consolidated hydrogen-bonding network.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}_2(\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_6)(\text{C}_{12}\text{H}_8\text{N}_2)_4] \cdot (\text{NO}_3)_2 \cdot \text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_6 \cdot 8\text{H}_2\text{O}$
M_r	1674.50
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	223
a, b, c (Å)	11.0448 (12), 13.0793 (15), 15.419 (2)
α, β, γ (°)	65.322 (10), 81.013 (11), 66.007 (8)
V (Å ³)	1848.8 (4)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.67
Crystal size (mm)	0.25 × 0.23 × 0.21
Data collection	
Diffractometer	Stoe <i>IPDS 2</i>
Absorption correction	Numerical (<i>X-AREA</i> , <i>X-RED32</i> ; Stoe, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.768, 0.791
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22995, 6493, 5435
R_{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.047 0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.052, 0.129, 1.04
No. of reflections	6493
No. of parameters	542
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.33, -0.70

Computer programs: *X-AREA* and *X-RED* (Stoe, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *DIAMOND* (Brandenburg 2007), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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supporting information

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Crystal structure and Hirshfeld surface analysis of (μ -2-{4-[(carboxylatomethyl)-carbamoyl]benzamido}acetato- κ^2 O:O'})bis[bis(1,10-phenanthroline- κ^2 N,N')copper(II)] dinitrate *N,N'*-(1,4-phenylenedicarbonyl)diglycine monosolvate octahydrate

Niels-Patrick Pook, Arnold Adam and Mimoza Gjika

Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-RED* (Stoe, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg 2007); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

(μ -2-{4-[(Carboxylatomethyl)carbamoyl]benzamido}acetato- κ^2 O:O'})bis[bis(1,10-phenanthroline- κ^2 N,N')copper(II)] dinitrate *N,N'*-(1,4-phenylenedicarbonyl)diglycine monosolvate octahydrate

Crystal data

[Cu₂(C₁₂H₁₀N₂O₆)(C₁₂H₈N₂)₄]
(NO₃)₂:C₁₂H₁₂N₂O₆·8H₂O

M_r = 1674.50

Triclinic, *P* $\bar{1}$

a = 11.0448 (12) Å

b = 13.0793 (15) Å

c = 15.419 (2) Å

α = 65.322 (10)°

β = 81.013 (11)°

γ = 66.007 (8)°

V = 1848.8 (4) Å³

Z = 1

F(000) = 866

D_x = 1.504 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 25382 reflections

θ = 4.0–62.1°

μ = 0.67 mm⁻¹

T = 223 K

Block, blue

0.25 × 0.23 × 0.21 mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4
mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: numerical

(*X-AREA*, *X-RED32*; Stoe, 2008)

T_{min} = 0.768, *T_{max}* = 0.791

22995 measured reflections

6493 independent reflections

5435 reflections with *I* > 2 σ (*I*)

R_{int} = 0.047

θ_{\max} = 25.0°, θ_{\min} = 2.0°

h = -13→13

k = -15→15

l = -18→18

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.129$ $S = 1.04$

6493 reflections

542 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 2.4056P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 1.33 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.70 \text{ e } \text{\AA}^{-3}$ *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	0.25718 (4)	0.21545 (4)	0.74008 (3)	0.03391 (13)
O1	0.3776 (3)	0.3298 (4)	0.6699 (2)	0.0753 (10)
O2	0.4964 (4)	0.1408 (4)	0.6874 (2)	0.0757 (10)
O3	0.8457 (3)	0.1118 (2)	0.69057 (17)	0.0501 (6)
O4	0.1969 (3)	0.7417 (3)	0.7625 (2)	0.0674 (9)
O5	0.1003 (4)	0.6311 (3)	0.7449 (3)	0.0756 (10)
H5	0.184 (6)	0.598 (6)	0.735 (4)	0.10 (2)*
O6	0.0556 (3)	0.7144 (2)	0.98070 (18)	0.0470 (6)
O7	0.5373 (3)	0.7260 (3)	0.7046 (2)	0.0658 (8)
O8	0.4738 (3)	0.7032 (3)	0.5920 (3)	0.0721 (9)
O9	0.4346 (3)	0.8821 (3)	0.5846 (3)	0.0763 (10)
O10	0.6564 (4)	0.8916 (4)	0.7169 (3)	0.0788 (11)
H10A	0.609 (7)	0.965 (7)	0.700 (5)	0.118*
H10B	0.601 (7)	0.860 (6)	0.720 (5)	0.118*
O11	0.3366 (4)	0.5419 (4)	0.6730 (4)	0.1124 (16)
H11A	0.377732	0.589890	0.649309	0.169*
H11B	0.372532	0.460190	0.669708	0.169*
O12	0.5209 (4)	0.5019 (4)	0.8692 (3)	0.0860 (12)
H12A	0.509 (8)	0.552 (7)	0.817 (6)	0.129*
H12B	0.456 (8)	0.509 (7)	0.901 (6)	0.129*
O13	0.3103 (4)	0.5241 (3)	1.0022 (3)	0.0735 (10)
H13A	0.340 (7)	0.514 (7)	1.047 (5)	0.110*
H13B	0.242 (7)	0.580 (6)	1.001 (5)	0.110*
N1	0.2860 (3)	0.2114 (2)	0.86480 (19)	0.0344 (6)
N2	0.2949 (2)	0.0293 (2)	0.82400 (18)	0.0316 (6)
N3	0.2122 (3)	0.2190 (3)	0.61963 (19)	0.0374 (6)
N4	0.0604 (3)	0.3436 (3)	0.7252 (2)	0.0383 (6)
N5	0.6970 (3)	0.2107 (3)	0.5731 (2)	0.0442 (7)
H5N	0.676 (4)	0.222 (4)	0.522 (3)	0.053*
N6	-0.0342 (3)	0.8618 (3)	0.8420 (2)	0.0403 (7)

H6	-0.060 (4)	0.928 (4)	0.809 (3)	0.048*
N7	0.4814 (3)	0.7715 (3)	0.6274 (3)	0.0527 (8)
C1	0.2822 (4)	0.3037 (3)	0.8825 (3)	0.0443 (8)
H1	0.267837	0.379334	0.831627	0.053*
C2	0.2987 (4)	0.2912 (4)	0.9743 (3)	0.0495 (9)
H2	0.293266	0.358439	0.985341	0.059*
C3	0.3229 (3)	0.1814 (4)	1.0482 (3)	0.0452 (9)
H3	0.334490	0.172589	1.110445	0.054*
C4	0.3306 (3)	0.0807 (3)	1.0318 (2)	0.0356 (7)
C5	0.3589 (3)	-0.0393 (4)	1.1040 (2)	0.0447 (9)
H5C	0.371489	-0.053382	1.167503	0.054*
C6	0.3681 (3)	-0.1326 (4)	1.0830 (3)	0.0453 (9)
H6C	0.387433	-0.210433	1.131931	0.054*
C7	0.3489 (3)	-0.1146 (3)	0.9879 (2)	0.0362 (7)
C8	0.3598 (3)	-0.2085 (3)	0.9613 (3)	0.0446 (8)
H8	0.381504	-0.288631	1.007015	0.054*
C9	0.3387 (3)	-0.1819 (3)	0.8691 (3)	0.0457 (9)
H9	0.346209	-0.243619	0.849851	0.055*
C10	0.3055 (3)	-0.0621 (3)	0.8023 (3)	0.0384 (7)
H10	0.289800	-0.045355	0.738683	0.046*
C11	0.3174 (3)	0.0027 (3)	0.9160 (2)	0.0291 (6)
C12	0.3098 (3)	0.1013 (3)	0.9378 (2)	0.0303 (6)
C13	0.2907 (4)	0.1582 (4)	0.5673 (3)	0.0443 (8)
H13	0.378778	0.107489	0.587836	0.053*
C14	0.2470 (4)	0.1674 (4)	0.4843 (3)	0.0505 (9)
H14	0.304078	0.123004	0.449269	0.061*
C15	0.1214 (4)	0.2409 (4)	0.4545 (3)	0.0539 (10)
H15	0.090157	0.247967	0.398148	0.065*
C16	0.0357 (4)	0.3078 (3)	0.5073 (3)	0.0460 (9)
C17	-0.0983 (4)	0.3896 (4)	0.4813 (3)	0.0599 (11)
H17	-0.134768	0.400995	0.425248	0.072*
C18	-0.1743 (4)	0.4512 (4)	0.5349 (3)	0.0597 (12)
H18	-0.262002	0.504503	0.514847	0.072*
C19	-0.1264 (3)	0.4381 (3)	0.6200 (3)	0.0489 (9)
C20	-0.2005 (4)	0.5012 (4)	0.6777 (4)	0.0607 (12)
H20	-0.289424	0.553980	0.661767	0.073*
C21	-0.1440 (4)	0.4859 (4)	0.7556 (3)	0.0601 (11)
H21	-0.191930	0.528552	0.794160	0.072*
C22	-0.0130 (4)	0.4056 (3)	0.7777 (3)	0.0486 (9)
H22	0.025920	0.394412	0.832696	0.058*
C23	0.0045 (3)	0.3590 (3)	0.6474 (2)	0.0370 (7)
C24	0.0857 (3)	0.2931 (3)	0.5906 (2)	0.0364 (7)
C25	0.8721 (3)	0.0698 (4)	0.4687 (3)	0.0458 (9)
H25	0.784492	0.117261	0.445384	0.055*
C26	1.0356 (3)	-0.0078 (4)	0.5836 (2)	0.0450 (9)
H26	1.062733	-0.014694	0.641321	0.054*
C27	0.9071 (3)	0.0624 (3)	0.5529 (2)	0.0341 (7)
C28	0.8138 (3)	0.1297 (3)	0.6120 (2)	0.0369 (7)

C29	0.6000 (3)	0.2888 (3)	0.6167 (3)	0.0441 (8)
H29A	0.565464	0.372051	0.568373	0.053*
H29B	0.644011	0.289430	0.666847	0.053*
C30	0.4828 (4)	0.2492 (5)	0.6605 (3)	0.0528 (10)
C31	0.0363 (3)	0.8779 (3)	1.0573 (2)	0.0357 (7)
H31	0.061328	0.794751	1.096732	0.043*
C32	-0.0312 (3)	1.0411 (3)	0.9051 (2)	0.0357 (7)
H32	-0.052282	1.069462	0.840293	0.043*
C33	0.0048 (3)	0.9183 (3)	0.9624 (2)	0.0318 (7)
C34	0.0115 (3)	0.8235 (3)	0.9290 (2)	0.0353 (7)
C35	-0.0341 (3)	0.7756 (4)	0.8067 (3)	0.0461 (9)
H35A	-0.100359	0.817367	0.755127	0.055*
H35B	-0.059411	0.712505	0.858186	0.055*
C36	0.1019 (4)	0.7156 (4)	0.7694 (3)	0.0563 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0328 (2)	0.0360 (2)	0.0307 (2)	-0.00752 (16)	-0.00332 (15)	-0.01511 (17)
O1	0.0422 (16)	0.131 (3)	0.0574 (18)	-0.0224 (18)	0.0062 (13)	-0.053 (2)
O2	0.106 (3)	0.099 (3)	0.0428 (16)	-0.075 (2)	-0.0118 (16)	-0.0072 (17)
O3	0.0499 (14)	0.0586 (17)	0.0344 (13)	-0.0057 (12)	-0.0082 (11)	-0.0230 (12)
O4	0.0387 (15)	0.101 (3)	0.0662 (19)	-0.0118 (15)	-0.0036 (13)	-0.0495 (19)
O5	0.069 (2)	0.071 (2)	0.093 (3)	-0.0012 (17)	-0.0093 (18)	-0.059 (2)
O6	0.0528 (14)	0.0393 (15)	0.0485 (15)	-0.0111 (12)	-0.0088 (12)	-0.0197 (12)
O7	0.0598 (17)	0.074 (2)	0.0545 (18)	-0.0071 (15)	-0.0100 (14)	-0.0307 (16)
O8	0.0640 (19)	0.081 (2)	0.083 (2)	-0.0173 (17)	-0.0116 (16)	-0.048 (2)
O9	0.0559 (18)	0.056 (2)	0.097 (3)	-0.0071 (15)	-0.0173 (17)	-0.0196 (19)
O10	0.072 (2)	0.114 (3)	0.066 (2)	-0.031 (2)	-0.0087 (17)	-0.051 (2)
O11	0.102 (3)	0.073 (3)	0.145 (4)	-0.017 (2)	0.042 (3)	-0.056 (3)
O12	0.080 (2)	0.066 (2)	0.082 (3)	-0.008 (2)	-0.017 (2)	-0.015 (2)
O13	0.062 (2)	0.0505 (19)	0.109 (3)	-0.0093 (15)	-0.0154 (19)	-0.038 (2)
N1	0.0352 (14)	0.0343 (15)	0.0353 (14)	-0.0101 (11)	-0.0006 (11)	-0.0177 (12)
N2	0.0283 (12)	0.0362 (15)	0.0320 (13)	-0.0099 (11)	-0.0002 (10)	-0.0168 (12)
N3	0.0344 (14)	0.0431 (17)	0.0327 (14)	-0.0112 (12)	-0.0031 (11)	-0.0151 (13)
N4	0.0328 (14)	0.0353 (15)	0.0381 (15)	-0.0087 (12)	0.0021 (12)	-0.0112 (12)
N5	0.0367 (15)	0.0496 (19)	0.0401 (16)	-0.0054 (13)	-0.0054 (13)	-0.0206 (15)
N6	0.0386 (15)	0.0457 (18)	0.0406 (17)	-0.0099 (14)	-0.0050 (12)	-0.0247 (14)
N7	0.0346 (15)	0.056 (2)	0.063 (2)	-0.0049 (15)	-0.0018 (15)	-0.0294 (19)
C1	0.051 (2)	0.039 (2)	0.049 (2)	-0.0165 (16)	0.0015 (16)	-0.0242 (17)
C2	0.048 (2)	0.057 (2)	0.063 (2)	-0.0208 (18)	0.0056 (18)	-0.043 (2)
C3	0.0381 (18)	0.068 (3)	0.045 (2)	-0.0213 (17)	0.0056 (15)	-0.038 (2)
C4	0.0261 (14)	0.054 (2)	0.0323 (16)	-0.0158 (14)	0.0006 (12)	-0.0208 (15)
C5	0.0358 (17)	0.067 (3)	0.0296 (17)	-0.0229 (17)	-0.0025 (13)	-0.0126 (17)
C6	0.0395 (18)	0.049 (2)	0.0352 (18)	-0.0175 (16)	-0.0076 (14)	-0.0023 (16)
C7	0.0288 (15)	0.0389 (19)	0.0378 (17)	-0.0143 (14)	-0.0017 (13)	-0.0103 (15)
C8	0.0388 (18)	0.0356 (19)	0.054 (2)	-0.0140 (15)	-0.0057 (16)	-0.0108 (17)
C9	0.0405 (18)	0.041 (2)	0.065 (2)	-0.0160 (16)	0.0023 (17)	-0.0298 (19)

C10	0.0352 (17)	0.044 (2)	0.0425 (18)	-0.0116 (14)	-0.0011 (14)	-0.0250 (16)
C11	0.0210 (13)	0.0348 (17)	0.0315 (15)	-0.0098 (12)	-0.0009 (11)	-0.0133 (13)
C12	0.0239 (14)	0.0376 (18)	0.0311 (16)	-0.0119 (13)	0.0010 (12)	-0.0150 (14)
C13	0.0409 (18)	0.054 (2)	0.0412 (19)	-0.0151 (16)	-0.0017 (15)	-0.0237 (17)
C14	0.060 (2)	0.067 (3)	0.0381 (19)	-0.031 (2)	0.0043 (17)	-0.0273 (19)
C15	0.069 (3)	0.066 (3)	0.0359 (19)	-0.038 (2)	-0.0098 (18)	-0.0132 (18)
C16	0.050 (2)	0.047 (2)	0.0390 (19)	-0.0273 (17)	-0.0134 (16)	-0.0024 (16)
C17	0.058 (2)	0.059 (3)	0.054 (2)	-0.028 (2)	-0.025 (2)	0.000 (2)
C18	0.043 (2)	0.049 (2)	0.069 (3)	-0.0169 (18)	-0.023 (2)	0.001 (2)
C19	0.0328 (17)	0.035 (2)	0.060 (2)	-0.0125 (15)	-0.0055 (16)	0.0001 (17)
C20	0.0341 (19)	0.044 (2)	0.082 (3)	-0.0043 (17)	-0.002 (2)	-0.013 (2)
C21	0.046 (2)	0.046 (2)	0.072 (3)	-0.0066 (18)	0.016 (2)	-0.026 (2)
C22	0.046 (2)	0.043 (2)	0.048 (2)	-0.0110 (16)	0.0069 (16)	-0.0168 (17)
C23	0.0332 (16)	0.0327 (18)	0.0368 (17)	-0.0137 (14)	-0.0030 (13)	-0.0037 (14)
C24	0.0364 (17)	0.0355 (18)	0.0326 (16)	-0.0170 (14)	-0.0055 (13)	-0.0038 (14)
C25	0.0313 (16)	0.060 (2)	0.0398 (19)	-0.0064 (16)	-0.0079 (14)	-0.0220 (18)
C26	0.0366 (17)	0.062 (2)	0.0346 (18)	-0.0093 (16)	-0.0069 (14)	-0.0236 (17)
C27	0.0332 (16)	0.0371 (18)	0.0292 (16)	-0.0132 (14)	-0.0012 (12)	-0.0100 (14)
C28	0.0350 (17)	0.0406 (19)	0.0335 (17)	-0.0163 (14)	0.0012 (13)	-0.0114 (15)
C29	0.0357 (17)	0.046 (2)	0.047 (2)	-0.0123 (15)	0.0040 (15)	-0.0196 (17)
C30	0.045 (2)	0.085 (3)	0.0306 (18)	-0.023 (2)	-0.0071 (15)	-0.023 (2)
C31	0.0375 (16)	0.0348 (18)	0.0329 (16)	-0.0127 (14)	-0.0050 (13)	-0.0108 (14)
C32	0.0369 (16)	0.0442 (19)	0.0272 (15)	-0.0142 (14)	-0.0027 (13)	-0.0152 (14)
C33	0.0240 (14)	0.0397 (18)	0.0334 (16)	-0.0095 (13)	0.0008 (12)	-0.0186 (14)
C34	0.0286 (15)	0.042 (2)	0.0384 (18)	-0.0111 (14)	0.0015 (13)	-0.0214 (16)
C35	0.0428 (19)	0.056 (2)	0.052 (2)	-0.0147 (17)	-0.0043 (16)	-0.0344 (19)
C36	0.062 (3)	0.054 (2)	0.040 (2)	0.005 (2)	-0.0153 (18)	-0.0273 (19)

Geometric parameters (Å, °)

Cu—N1	1.974 (3)	C6—H6C	0.9400
Cu—N3	1.974 (3)	C7—C11	1.404 (5)
Cu—N4	2.111 (3)	C7—C8	1.406 (5)
Cu—N2	2.119 (3)	C8—C9	1.350 (5)
Cu—O1	2.235 (4)	C8—H8	0.9400
O1—C30	1.249 (5)	C9—C10	1.397 (5)
O2—C30	1.249 (6)	C9—H9	0.9400
O3—C28	1.214 (4)	C10—H10	0.9400
O4—C36	1.205 (6)	C11—C12	1.431 (4)
O5—C36	1.316 (5)	C13—C14	1.379 (5)
O5—H5	0.87 (6)	C13—H13	0.9400
O6—C34	1.231 (4)	C14—C15	1.344 (6)
O7—N7	1.221 (4)	C14—H14	0.9400
O8—N7	1.259 (5)	C15—C16	1.415 (6)
O9—N7	1.224 (5)	C15—H15	0.9400
O10—H10A	0.83 (7)	C16—C24	1.387 (5)
O10—H10B	0.85 (7)	C16—C17	1.426 (6)
O11—H11A	0.8498	C17—C18	1.352 (7)

O11—H11B	0.9981	C17—H17	0.9400
O12—H12A	0.79 (8)	C18—C19	1.408 (6)
O12—H12B	0.80 (8)	C18—H18	0.9400
O13—H13A	0.75 (7)	C19—C23	1.395 (5)
O13—H13B	0.81 (7)	C19—C20	1.408 (6)
N1—C1	1.328 (4)	C20—C21	1.343 (7)
N1—C12	1.357 (4)	C20—H20	0.9400
N2—C10	1.328 (4)	C21—C22	1.390 (6)
N2—C11	1.350 (4)	C21—H21	0.9400
N3—C13	1.338 (5)	C22—H22	0.9400
N3—C24	1.350 (4)	C23—C24	1.439 (5)
N4—C22	1.334 (5)	C25—C27	1.366 (5)
N4—C23	1.338 (4)	C25—C26 ⁱ	1.401 (5)
N5—C28	1.322 (4)	C25—H25	0.9400
N5—C29	1.450 (5)	C26—C27	1.368 (5)
N5—H5N	0.79 (4)	C26—H26	0.9400
N6—C34	1.324 (4)	C27—C28	1.519 (5)
N6—C35	1.440 (5)	C29—C30	1.542 (5)
N6—H6	0.75 (4)	C29—H29A	0.9800
C1—C2	1.389 (5)	C29—H29B	0.9800
C1—H1	0.9400	C31—C33	1.381 (4)
C2—C3	1.360 (6)	C31—C32 ⁱⁱ	1.385 (5)
C2—H2	0.9400	C31—H31	0.9400
C3—C4	1.410 (5)	C32—C33	1.387 (5)
C3—H3	0.9400	C32—H32	0.9400
C4—C12	1.397 (4)	C33—C34	1.500 (5)
C4—C5	1.432 (5)	C35—C36	1.533 (5)
C5—C6	1.350 (6)	C35—H35A	0.9800
C5—H5C	0.9400	C35—H35B	0.9800
C6—C7	1.420 (5)		
N1—Cu—N3	174.71 (11)	C15—C14—C13	118.7 (4)
N1—Cu—N4	93.74 (11)	C15—C14—H14	120.6
N3—Cu—N4	82.45 (11)	C13—C14—H14	120.6
N1—Cu—N2	81.30 (11)	C14—C15—C16	120.6 (3)
N3—Cu—N2	97.30 (11)	C14—C15—H15	119.7
N4—Cu—N2	118.90 (10)	C16—C15—H15	119.7
N1—Cu—O1	90.02 (11)	C24—C16—C15	117.6 (3)
N3—Cu—O1	94.44 (11)	C24—C16—C17	117.3 (4)
N4—Cu—O1	103.88 (12)	C15—C16—C17	125.1 (4)
N2—Cu—O1	136.69 (11)	C18—C17—C16	121.9 (4)
C30—O1—Cu	98.7 (3)	C18—C17—H17	119.0
C36—O5—H5	99 (4)	C16—C17—H17	119.0
H10A—O10—H10B	103 (7)	C17—C18—C19	122.1 (4)
H11A—O11—H11B	121.6	C17—C18—H18	119.0
H12A—O12—H12B	114 (8)	C19—C18—H18	119.0
H13A—O13—H13B	99 (7)	C23—C19—C20	118.0 (4)
C1—N1—C12	119.3 (3)	C23—C19—C18	117.5 (4)

C1—N1—Cu	126.8 (2)	C20—C19—C18	124.4 (4)
C12—N1—Cu	113.9 (2)	C21—C20—C19	119.9 (4)
C10—N2—C11	117.0 (3)	C21—C20—H20	120.1
C10—N2—Cu	132.6 (2)	C19—C20—H20	120.1
C11—N2—Cu	110.3 (2)	C20—C21—C22	118.4 (4)
C13—N3—C24	119.5 (3)	C20—C21—H21	120.8
C13—N3—Cu	127.8 (2)	C22—C21—H21	120.8
C24—N3—Cu	112.7 (2)	N4—C22—C21	123.5 (4)
C22—N4—C23	118.1 (3)	N4—C22—H22	118.2
C22—N4—Cu	132.7 (3)	C21—C22—H22	118.2
C23—N4—Cu	109.1 (2)	N4—C23—C19	122.0 (3)
C28—N5—C29	123.9 (3)	N4—C23—C24	117.4 (3)
C28—N5—H5N	121 (3)	C19—C23—C24	120.6 (3)
C29—N5—H5N	115 (3)	N3—C24—C16	121.2 (3)
C34—N6—C35	120.2 (3)	N3—C24—C23	118.3 (3)
C34—N6—H6	122 (3)	C16—C24—C23	120.6 (3)
C35—N6—H6	118 (3)	C27—C25—C26 ⁱ	121.2 (3)
O7—N7—O9	120.3 (4)	C27—C25—H25	119.4
O7—N7—O8	119.2 (4)	C26 ⁱ —C25—H25	119.4
O9—N7—O8	120.4 (4)	C27—C26—C25 ⁱ	121.7 (3)
N1—C1—C2	121.7 (4)	C27—C26—H26	119.2
N1—C1—H1	119.2	C25 ⁱ —C26—H26	119.2
C2—C1—H1	119.2	C25—C27—C26	117.1 (3)
C3—C2—C1	119.7 (3)	C25—C27—C28	124.2 (3)
C3—C2—H2	120.1	C26—C27—C28	118.6 (3)
C1—C2—H2	120.1	O3—C28—N5	121.5 (3)
C2—C3—C4	120.1 (3)	O3—C28—C27	121.8 (3)
C2—C3—H3	119.9	N5—C28—C27	116.8 (3)
C4—C3—H3	119.9	N5—C29—C30	113.6 (3)
C12—C4—C3	116.7 (3)	N5—C29—H29A	108.8
C12—C4—C5	118.8 (3)	C30—C29—H29A	108.8
C3—C4—C5	124.5 (3)	N5—C29—H29B	108.8
C6—C5—C4	121.6 (3)	C30—C29—H29B	108.8
C6—C5—H5C	119.2	H29A—C29—H29B	107.7
C4—C5—H5C	119.2	O2—C30—O1	123.1 (4)
C5—C6—C7	120.8 (3)	O2—C30—C29	120.4 (4)
C5—C6—H6C	119.6	O1—C30—C29	116.5 (4)
C7—C6—H6C	119.6	C33—C31—C32 ⁱⁱ	120.4 (3)
C11—C7—C8	117.6 (3)	C33—C31—H31	119.8
C11—C7—C6	118.9 (3)	C32 ⁱⁱ —C31—H31	119.8
C8—C7—C6	123.5 (3)	C31 ⁱⁱ —C32—C33	120.5 (3)
C9—C8—C7	119.0 (3)	C31 ⁱⁱ —C32—H32	119.7
C9—C8—H8	120.5	C33—C32—H32	119.7
C7—C8—H8	120.5	C31—C33—C32	119.0 (3)
C8—C9—C10	119.7 (3)	C31—C33—C34	116.3 (3)
C8—C9—H9	120.2	C32—C33—C34	124.6 (3)
C10—C9—H9	120.2	O6—C34—N6	120.8 (3)
N2—C10—C9	123.5 (3)	O6—C34—C33	121.7 (3)

N2—C10—H10	118.2	N6—C34—C33	117.4 (3)
C9—C10—H10	118.2	N6—C35—C36	112.1 (3)
N2—C11—C7	123.3 (3)	N6—C35—H35A	109.2
N2—C11—C12	116.4 (3)	C36—C35—H35A	109.2
C7—C11—C12	120.3 (3)	N6—C35—H35B	109.2
N1—C12—C4	122.5 (3)	C36—C35—H35B	109.2
N1—C12—C11	118.0 (3)	H35A—C35—H35B	107.9
C4—C12—C11	119.5 (3)	O4—C36—O5	124.3 (4)
N3—C13—C14	122.4 (3)	O4—C36—C35	125.6 (4)
N3—C13—H13	118.8	O5—C36—C35	110.0 (4)
C14—C13—H13	118.8		
C12—N1—C1—C2	-1.6 (5)	C23—N4—C22—C21	-0.5 (6)
Cu—N1—C1—C2	177.3 (3)	Cu—N4—C22—C21	-179.0 (3)
N1—C1—C2—C3	1.7 (6)	C20—C21—C22—N4	0.7 (6)
C1—C2—C3—C4	-0.2 (5)	C22—N4—C23—C19	0.6 (5)
C2—C3—C4—C12	-1.2 (5)	Cu—N4—C23—C19	179.4 (3)
C2—C3—C4—C5	178.3 (3)	C22—N4—C23—C24	178.9 (3)
C12—C4—C5—C6	1.1 (5)	Cu—N4—C23—C24	-2.2 (4)
C3—C4—C5—C6	-178.3 (3)	C20—C19—C23—N4	-0.9 (5)
C4—C5—C6—C7	-0.4 (5)	C18—C19—C23—N4	177.7 (3)
C5—C6—C7—C11	-1.3 (5)	C20—C19—C23—C24	-179.2 (3)
C5—C6—C7—C8	178.7 (3)	C18—C19—C23—C24	-0.6 (5)
C11—C7—C8—C9	-0.5 (5)	C13—N3—C24—C16	-0.2 (5)
C6—C7—C8—C9	179.5 (3)	Cu—N3—C24—C16	179.8 (3)
C7—C8—C9—C10	-0.5 (5)	C13—N3—C24—C23	-178.8 (3)
C11—N2—C10—C9	-0.2 (5)	Cu—N3—C24—C23	1.3 (4)
Cu—N2—C10—C9	176.2 (2)	C15—C16—C24—N3	1.0 (5)
C8—C9—C10—N2	1.0 (5)	C17—C16—C24—N3	-178.9 (3)
C10—N2—C11—C7	-0.9 (4)	C15—C16—C24—C23	179.5 (3)
Cu—N2—C11—C7	-178.1 (2)	C17—C16—C24—C23	-0.4 (5)
C10—N2—C11—C12	178.1 (3)	N4—C23—C24—N3	0.8 (5)
Cu—N2—C11—C12	0.8 (3)	C19—C23—C24—N3	179.1 (3)
C8—C7—C11—N2	1.3 (4)	N4—C23—C24—C16	-177.8 (3)
C6—C7—C11—N2	-178.7 (3)	C19—C23—C24—C16	0.6 (5)
C8—C7—C11—C12	-177.6 (3)	C26 ⁱ —C25—C27—C26	0.0 (6)
C6—C7—C11—C12	2.4 (4)	C26 ⁱ —C25—C27—C28	178.1 (3)
C1—N1—C12—C4	0.0 (4)	C25 ⁱ —C26—C27—C25	0.0 (6)
Cu—N1—C12—C4	-178.9 (2)	C25 ⁱ —C26—C27—C28	-178.3 (3)
C1—N1—C12—C11	-178.1 (3)	C29—N5—C28—O3	3.2 (6)
Cu—N1—C12—C11	2.9 (3)	C29—N5—C28—C27	-175.6 (3)
C3—C4—C12—N1	1.3 (4)	C25—C27—C28—O3	173.1 (4)
C5—C4—C12—N1	-178.2 (3)	C26—C27—C28—O3	-8.8 (5)
C3—C4—C12—C11	179.5 (3)	C25—C27—C28—N5	-8.2 (5)
C5—C4—C12—C11	0.0 (4)	C26—C27—C28—N5	170.0 (3)
N2—C11—C12—N1	-2.5 (4)	C28—N5—C29—C30	-104.5 (4)
C7—C11—C12—N1	176.5 (3)	Cu—O1—C30—O2	0.1 (4)
N2—C11—C12—C4	179.3 (3)	Cu—O1—C30—C29	-177.7 (3)

C7—C11—C12—C4	-1.7 (4)	N5—C29—C30—O2	25.4 (5)
C24—N3—C13—C14	-0.6 (6)	N5—C29—C30—O1	-156.7 (3)
Cu—N3—C13—C14	179.3 (3)	C32 ⁱⁱ —C31—C33—C32	0.4 (5)
N3—C13—C14—C15	0.6 (6)	C32 ⁱⁱ —C31—C33—C34	-179.2 (3)
C13—C14—C15—C16	0.1 (6)	C31 ⁱⁱ —C32—C33—C31	-0.4 (5)
C14—C15—C16—C24	-0.9 (6)	C31 ⁱⁱ —C32—C33—C34	179.1 (3)
C14—C15—C16—C17	179.0 (4)	C35—N6—C34—O6	0.6 (5)
C24—C16—C17—C18	0.3 (6)	C35—N6—C34—C33	-178.2 (3)
C15—C16—C17—C18	-179.6 (4)	C31—C33—C34—O6	-7.2 (4)
C16—C17—C18—C19	-0.3 (7)	C32—C33—C34—O6	173.3 (3)
C17—C18—C19—C23	0.5 (6)	C31—C33—C34—N6	171.6 (3)
C17—C18—C19—C20	179.0 (4)	C32—C33—C34—N6	-8.0 (5)
C23—C19—C20—C21	1.2 (6)	C34—N6—C35—C36	-81.3 (4)
C18—C19—C20—C21	-177.3 (4)	N6—C35—C36—O4	-5.3 (6)
C19—C20—C21—C22	-1.1 (6)	N6—C35—C36—O5	175.1 (3)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O11	0.87 (6)	1.84 (6)	2.665 (5)	159 (6)
O10—H10A \cdots O2 ⁱⁱⁱ	0.83 (7)	2.06 (7)	2.878 (6)	168 (7)
O10—H10B \cdots O7	0.85 (7)	2.24 (7)	3.033 (6)	155 (7)
O11—H11A \cdots O8	0.85	2.00	2.848 (6)	179
O11—H11B \cdots O1	1.00	1.68	2.643 (6)	160
O12—H12A \cdots O7	0.79 (8)	2.32 (8)	3.024 (6)	149 (8)
O12—H12B \cdots O13	0.80 (8)	2.07 (8)	2.856 (6)	170 (8)
O13—H13A \cdots O12 ^{iv}	0.75 (7)	2.05 (7)	2.757 (6)	157 (8)
O13—H13B \cdots O6	0.81 (7)	2.05 (7)	2.851 (4)	170 (7)
N5—H5N \cdots O8 ^v	0.79 (4)	2.23 (5)	2.947 (4)	152 (4)
N6—H6 \cdots O3 ^{vi}	0.75 (4)	2.26 (4)	2.995 (4)	167 (4)
C2—H2 \cdots O13	0.94	2.37	3.302 (5)	172
C3—H3 \cdots O10 ^{iv}	0.94	2.44	3.358 (7)	165
C9—H9 \cdots O4 ^{vii}	0.94	2.40	3.099 (5)	131
C13—H13 \cdots O2	0.94	2.42	3.031 (5)	122
C14—H14 \cdots O10 ^v	0.94	2.60	3.414 (5)	145
C25—H25 \cdots O9 ^v	0.94	2.53	3.354 (6)	147
C32—H32 \cdots O3 ^{vi}	0.94	2.48	3.388 (4)	163
C35—H35A \cdots O10 ^{viii}	0.98	2.53	3.378 (5)	145

Symmetry codes: (iii) $x, y+1, z$; (iv) $-x+1, -y+1, -z+2$; (v) $-x+1, -y+1, -z+1$; (vi) $x-1, y+1, z$; (vii) $x, y-1, z$; (viii) $x-1, y, z$.