Synthesis and crystal structure of trans-diaqua-(1,4,8,11-tetraazaundecane)copper(II) isophthalate monohydrate

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In the title hydrated molecular salt, \([\text{Cu(C}_7\text{H}_{20}\text{N}_4\text{(H}_2\text{O})_2\text{]}\text{(C}_8\text{H}_4\text{O}_4\text{)}\text{H}_2\text{O}]\), the metal ion is coordinated by the two primary and two secondary N atoms of the amine ligand and the mutually trans O atoms of the water molecules in a tetragonally distorted octahedral geometry. The average equatorial Cu—N bond lengths (2.013 and 2.026 Å for Cu—N_{prim} and Cu—N_{sec}, respectively) are substantially shorter than the average axial Cu—O bond length (2.518 Å). The tetraamine ligand adopts its energetically favored conformation with its five- and six-membered chelate rings in gauche and chair conformations, respectively. In the crystal, the N—H donor groups of the tetraamine, the acceptor carboxylate groups of the isophthalate dianion and both the coordinated water molecules and the water molecule of crystallization are involved in numerous N—H/C1/C1/C1O and O—H/C1/C1/C1O hydrogen bonds, resulting in the formation of electroneutral layers oriented parallel to the ac plane.

1. Chemical context

The copper(II) and nickel(II) complexes of tetradentateaza-macrocyclic ligands, in particular, cyclam and its structural analogues (cyclam = 1,4,8,11-tetraazaacyclotetradecane, C_{10}H_{24}N_{4}), are widely used for the construction of metal–organic frameworks (MOFs) based on oligocarboxylate linkers, which possess many promising applications (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh et al., 2012; Stackhouse & Ma, 2018; Lee & Moon, 2018). At the same time, open-chain aliphatic tetraamines like \(L\) (\(L = 1,4,8,11\)-tetraazaundecane, C_{7}H_{20}N_{4}), which is the closest structural and electronic analogue of cyclam, are practically unexploited in this respect and only one work dealing with the crystal structures of MOFs formed by the [Ni(\(L\))]^{2+} cation with tris(4-carboxylatobenzyl)amine has been reported to date (Jiang et al., 2012). Besides, the [\(M(L)\)] synthons (\(M = \text{Cu}^{II}, \text{Ni}^{II}\)) are convenient precursors for the one-pot template preparation of corresponding metal complexes of 14-membered azacyclam macrocycles (azacyclam = 1,4,8,11,13-pentaazaacyclotetradecane) (Rosokha et al., 1993; Gerbeleu et al., 1999) and some complexes of this type functionalized at the N_{13} position of the macrocyclic backbone have been structurally characterized by our group (Andriichuk et al., 2019; Tsymbal et al., 2010, 2021). Herein, we report the syntheses and crystal structure of the product of the reaction of CuCl_{2}, \(L\) and the isophthalate anion (ip^2−) as its sodium salt, namely, trans-diaqua(1,4,8,11-tetraazaundecane-x^2N_{11},N_{13},N_{16},N_{19}^1)-copper(II) isophthalate monohydrate, [Cu(\(L\))(H_{2}O)_{2}](ip)·H_{2}O. I.
2. Structural commentary

The asymmetric unit of the title hydrated molecular salt I consists of a complex di-cation \([Cu(L)(H_2O)]_{2}^{2+}\), a non-coordinated isophthalate di-anion \(ip_2^-\) and one water molecule of crystallization (Fig. 1). The Cu II ion is coordinated in the equatorial plane by the two primary and two secondary N atoms of the amine ligand in a nearly square-planar fashion (the deviations of the N atoms from the mean N4 plane are 0.006 Å), and by the two O atoms from the water molecules in the axial positions.

The average equatorial Cu—N prim bond length for N1 and N4 (2.013 Å) is slightly shorter than Cu—N sec one for N2 and N3 (2.025 Å), probably reflecting the stronger donating ability of the N atoms of primary versus secondary amine groups (Table 1). The average axial Cu—O bond length (2.518 Å) is substantially longer than the equatorial Cu—N bonds, which is likely due to a large Jahn–Teller distortion inherent in metal ions with a \(d^9\) electronic configuration. It is noteworthy that the Cu—O distances in I differ considerably (Table 1) and the CuII ion is displaced from the mean N4 plane of the ligand by 0.082 Å towards the O1W water molecule.

The ligand L in I adopts its energetically favored conformation with the five-membered chelate rings in gauche [average bite angle 85.74°] and six-membered chelate ring in chair conformations, which resemble the trans-III conformation usually observed in cyclam complexes (Barefield et al., 1986; Bosnich et al., 1965). The pseudo ‘bite’ angle formed by the primary amine donors N1—Cu1—N4 is slightly larger than that for N2—Cu1—N3 (Table 1).

The isophthalate di-anion in the title compound counter-balances the charge of the complex cation. The mean planes of the pendant carboxylate groups are slightly tilted relative to the mean plane of the aromatic ring [average angle = 9.8°]. The C—O bond lengths in the carboxylate groups are nearly equal (Table 1), thus indicating essentially complete electron delocalization.

3. Supramolecular features

In the crystal of I, the complex cation \([Cu(L)(H_2O)]_{2}^{2+}\), isophthalate anion \(ip_2^-\) and both coordinated water molecules and water molecule of crystallization are linked by numerous hydrogen bonds (Table 2), resulting in its distinct lamellar structure. In particular, hydrogen-bonding interactions between the N1, N2 and N3 amine groups and O1W and O2W water molecules as the donors and carboxylate atoms O1, O3 and O4 as the acceptors result in the formation of electro-neutral sheets (Fig. 2). Additionally, due to hydrogen bonds N4—H4A···O3 (−x + 1, −y + 1, −z + 1) and N1—H1A···O2W (−x, −y + 1, −z + 1) and four bonds formed by the water molecule O3W these sheets double into bilayers oriented parallel to the ac plane (Fig. 3). It is noteworthy that all the polar groups in I are saturated from the point of view of the number of possible hydrogen bonds, which equal to 2, 1, 2, 4 and 2 for the primary, secondary amine groups, coordinated water molecule, water molecule of crystallization and carboxylate O atoms, respectively.
There are no hydrogen-bonding contacts between the layers in I (Fig. 3). The three-dimensional coherence of the crystal is provided by van der Waals interactions between the methine and methylene fragments of the constituents.

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

| D—H · · ·A | D—H | H · · ·A | D · · ·A | D—H · · ·A |
|------------|------|---------|----------|------------|
| N1—H1A···O2Wvi | 0.97 | 2.30 | 3.143 (2) | 145 |
| N1—H1B···O3vi | 0.97 | 2.07 | 3.007 (2) | 161 |
| N2—H2···O4ivy | 0.98 | 1.95 | 2.907 (2) | 163 |
| N3—H3···O1 | 0.98 | 2.19 | 3.063 (3) | 148 |
| N4—H4A···O3vim | 0.97 | 2.10 | 3.042 (2) | 163 |
| O1W—H1WA···O1vii | 0.87 | 1.89 | 2.760 (2) | 174 |
| O2W—H2WA···O3vim | 0.87 | 2.09 | 2.930 (2) | 161 |
| O2W—H2WB···O3W | 0.87 | 2.00 | 2.872 (2) | 175 |
| O3W—H3WA···O2vi | 0.87 | 2.00 | 2.823 (2) | 157 |
| O3W—H3WB···O2 | 0.87 | 1.85 | 2.712 (2) | 174 |

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

**Figure 3**
Side view of the bilayers in I along the c axis. C-bound H atoms and coordinated water molecules have been omitted, hydrogen bonds are shown as dashed lines.

**Table 3**
Experimental details.

Crystal data
Chemical formula | [Cu(C7H20N4)(H2O)2](C8H4O4) | 2H2O |
|------------------|-----------------------------|-------|
| Mz               | 441.97                      |       |
| Crystal system, space group | Monoclinic, P21/c | |
| Temperature (K)  | 100                         |       |
| a, b, c (Å)      | 11.4727 (8), 24.1694 (18), 7.1591 (5) |
| β (°)            | 96.679 (4)                  |       |
| V (Å³)           | 1971.7 (2)                  |       |
| Z                 | 4                           |       |
| Radiation type   | Mo Ka                       |       |
| μ (mm⁻¹)         | 1.15                        |       |
| Crystal size (mm) | 0.15 × 0.15 × 0.06           |       |

Data collection
Diffractometer | Bruker APEXII CCD |
Absorption correction | Multi-scan (SADABS; Krause et al., 2015) |
|------------------|-------------------|
| Tmcr, Tmcr       | 0.846, 0.934      |
| No. of measurements, independent and observed | 53784, 3698, 3232 |
| Rmax            | 0.050             |
| (sin θ/λ)max (Å⁻¹) | 0.608           |

Refinement
R(F² > 2σ(F²)), wR(F²), S | 0.032, 0.079, 1.11 |
|---------------------------|-------------------|
| No. of reflections        | 3698              |
| No. of parameters         | 248               |
| No. of restraints         | 11                |
| H-atom treatment          | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³)     | 0.50, −0.32       |

Computer programs: APEX2 and SAINT (Bruker, 2012), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and pubCIF (Westrip, 2010).

4. Database survey
A search of the Cambridge Structural Database (CSD, version 5.43, last update March 2022; Groom et al., 2016) gave nine hits related to the compounds formed by the [Cu(L)]²⁺ core. Among them, the trans-CuN₄O₂ chromophores are characteristic of three complexes [CSD refcodes DAFYOA (Heeg et al., 2010), FICDEA (Lawrance et al., 1987) and TECCUA (Fawcett et al., 1980)] all of which contain coordinated perchlorate anions. Thus, the present work is the first structural characterization of a Cu¹ diaqua complex of this open-chain tetraamine.

In general, conformations of the amine ligand and geometrical parameters of coordination polyhedra in both types of cations are similar, even though the axial Cu—O bond lengths in the perchlorate complexes are longer. This can be explained by poorer donating ability of this anion as compared to aqua ligand. As in I, the Cu—O distances in previously mentioned compounds are non-equivalent even though the differences between them are smaller than in I and do not exceed 0.14 Å.

5. Synthesis and crystallization
All chemicals and solvents used in this work were purchased from Sigma–Aldrich and used without further purification.
The title compound I was prepared as follows. A solution of Na₂ip (105 mg, 0.5 mmol) in water (5 ml) was added to a solution of CuCl₂·2H₂O (85 mg, 0.5 mmol) and L (80 mg, 0.5 mmol) in water (5 ml). The blue precipitate, which formed in several days, was filtered off, washed with methanol (2 ml) and diethyl ether and dried in air. Yield: 106 mg (48%). Analysis calculated for C₁₅H₃₀CuN₄O₇: C 40.76, H 6.84, N 12.67%. Found: C 40.56, H 6.96, N 12.42%. Single crystals of I of X-ray diffraction quality were selected from the sample resulting from the synthesis.

6. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms in I were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (ring H atoms) or 0.99 Å (aliphatic H atoms), N—H distances of 0.97 (primary amine groups) or 0.98 Å (secondary amine groups) with U₁₀(H) values of 1.2Uₑq of the parent atoms. Water H atoms were positioned geometrically (O—H distances of 0.87 Å) and refined as riding with U₁₀(H) = 1.5Uₑq(O).

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Synthesis and crystal structure of \textit{trans}-diaqua(1,4,8,11-tetraazaundecane)-copper(II) isophthalate monohydrate

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Computing details

Data collection: \textit{APEX2} (Bruker, 2012); cell refinement: \textit{SAINT} (Bruker, 2012); data reduction: \textit{SAINT} (Bruker, 2012); program(s) used to solve structure: \textit{SHELXT2018/2} (Sheldrick, 2015a); program(s) used to refine structure: \textit{SHELXL2018/3} (Sheldrick, 2015b); molecular graphics: \textit{Mercury} (Macrae et al., 2020); software used to prepare material for publication: \textit{publCIF} (Westrip, 2010).

\textit{trans}-Diaqua(1,4,8,11-tetraazaundecane-κ\textsubscript{4}N\textsubscript{1},N\textsubscript{4},N\textsubscript{8},N\textsubscript{11})copper(II) benzene-1,3-dicarboxylate monohydrate

Crystal data

\begin{verbatim}
[Cu(C\textsubscript{7}H\textsubscript{20}N\textsubscript{4})(H\textsubscript{2}O)\textsubscript{2}](C\textsubscript{8}H\textsubscript{4}O\textsubscript{4})\cdot H\textsubscript{2}O

F(000) = 932
D\textsubscript{x} = 1.489 Mg m\textsuperscript{-3}
Mo Ka radiation, \(\lambda = 0.71073\) Å

Cell parameters from 2350 reflections

\(\theta = 2.0-25.0^\circ\)
\(\mu = 1.15\) mm\textsuperscript{-1}
\(T = 100\) K
Prism, light blue
0.15 × 0.15 × 0.06 mm

\end{verbatim}

Data collection

\begin{verbatim}
Bruker APEXII CCD
diffractometer
\(\varphi\) and \(\omega\) scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)

3698 independent reflections
3232 reflections with \(I > 2\sigma(I)\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.032\)
\(wR(F^2) = 0.079\)
\(S = 1.11\)
3698 reflections
248 parameters
11 restraints
Primary atom site location: dual

Hydrogen site location: mixed
\(H\) atoms treated by a mixture of independent and constrained refinement

\(w = 1/[\sigma^2(F_c^2) + (0.0332P)^2 + 1.9773P]\)
where \(P = (F^2 + 2F_c^2)/3\)

\((\Delta\sigma)_{\text{max}} = 0.001\)
\(\Delta\rho_{\text{max}} = 0.50\) e Å\textsuperscript{-3}
\(\Delta\rho_{\text{min}} = -0.32\) e Å\textsuperscript{-3}

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

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

| Atom | x     | y     | z     | Uiso/Ut   |
|------|-------|-------|-------|-----------|
| Cu1  | 0.16222 (2) | 0.41162 (2) | 0.30691 (4) | 0.01549 (9) |
| O1W  | 0.19539 (13) | 0.37755 (7)  | 0.0057 (2)   | 0.0222 (4)  |
| H1WB | 0.140042 | 0.364422 | −0.075635 | 0.033* |
| H1WA | 0.262802 | 0.372482 | −0.036104 | 0.033* |
| N1   | 0.00154 (16) | 0.44151 (8)  | 0.2133 (3)   | 0.0187 (4)  |
| H1B  | −0.009406 | 0.441387 | 0.076913 | 0.022* |
| H1A  | −0.008806 | 0.479637 | 0.250343 | 0.022* |
| N2   | 0.07640 (16) | 0.34306 (8)  | 0.3776 (3)   | 0.0162 (4)  |
| H2   | 0.070058 | 0.343234 | 0.512940 | 0.019* |
| N3   | 0.31993 (16) | 0.38284 (8)  | 0.4245 (3)   | 0.0173 (4)  |
| H3   | 0.320619 | 0.384199 | 0.561434 | 0.021* |
| N4   | 0.24838 (16) | 0.48139 (8)  | 0.2576 (3)   | 0.0185 (4)  |
| H4B  | 0.207629 | 0.515358 | 0.281406 | 0.022* |
| H4A  | 0.264879 | 0.480508 | 0.127836 | 0.022* |
| C1   | −0.0875 (2) | 0.40536 (10) | 0.2874 (3)   | 0.0225 (5)  |
| H1C  | −0.164157 | 0.409352 | 0.209563 | 0.027* |
| H1D  | −0.097246 | 0.415929 | 0.418270 | 0.027* |
| C2   | −0.04516 (19) | 0.34645 (10) | 0.2813 (3)   | 0.0210 (5)  |
| H2A  | −0.097361 | 0.321866 | 0.344534 | 0.025* |
| H2B  | −0.046743 | 0.334230 | 0.148997 | 0.025* |
| C3   | 0.1331 (2) | 0.28961 (10) | 0.3430 (3)   | 0.0208 (5)  |
| H3A  | 0.138014 | 0.285553 | 0.206536 | 0.025* |
| H3B  | 0.084020 | 0.259027 | 0.382426 | 0.025* |
| C4   | 0.2563 (2) | 0.28505 (10) | 0.4492 (3)   | 0.0223 (5)  |
| H4C  | 0.251528 | 0.292366 | 0.584128 | 0.027* |
| H4D  | 0.284504 | 0.246613 | 0.438010 | 0.027* |
| C5   | 0.3461 (2) | 0.32440 (10) | 0.3804 (3)   | 0.0213 (5)  |
| H5A  | 0.425481 | 0.314656 | 0.440994 | 0.026* |
| H5B  | 0.345745 | 0.320183 | 0.242808 | 0.026* |
| C6   | 0.4108 (2) | 0.42145 (10) | 0.3695 (3)   | 0.0214 (5)  |
| H6A  | 0.429531 | 0.412384 | 0.241485 | 0.026* |
| H6B  | 0.483487 | 0.417883 | 0.457819 | 0.026* |
| C7   | 0.3643 (2) | 0.48003 (10) | 0.3738 (3)   | 0.0216 (5)  |
| H7A  | 0.355909 | 0.491074 | 0.504759 | 0.026* |
| H7B  | 0.419204 | 0.506014 | 0.322469 | 0.026* |
| O1   | 0.39258 (13) | 0.35317 (7)  | 0.8377 (2)   | 0.0242 (4)  |
| O2   | 0.50998 (14) | 0.42314 (7)  | 0.9402 (2)   | 0.0241 (4)  |
| O3   | 0.92569 (13) | 0.42289 (7)  | 0.8018 (2)   | 0.0199 (4)  |
| O4   | 1.00945 (13) | 0.34100 (7)  | 0.7569 (2)   | 0.0215 (4)  |
| Atomic displacement parameters ($\AA^2$) |
|----------------------------------------|
|                                | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| Cu1                                 | 0.01437 (15) | 0.01537 (15) | 0.01669 (15) | −0.00035 (10) | 0.00163 (10) | 0.00072 (11) |
| O1W                                 | 0.0143 (8) | 0.0350 (10) | 0.0176 (8) | −0.0001 (7) | 0.0028 (6) | −0.0051 (7) |
| N1                                  | 0.0202 (10) | 0.0174 (10) | 0.0180 (10) | 0.0036 (8) | −0.0001 (8) | −0.0015 (8) |
| N2                                  | 0.0166 (9) | 0.0184 (10) | 0.0138 (9) | −0.0012 (7) | 0.0025 (7) | −0.0009 (7) |
| N3                                  | 0.0173 (9) | 0.0188 (10) | 0.0158 (10) | 0.0003 (8) | 0.0025 (7) | 0.0005 (8) |
| N4                                  | 0.0231 (10) | 0.0155 (10) | 0.0173 (10) | −0.0019 (8) | 0.0039 (8) | −0.0003 (8) |
| C1                                  | 0.0154 (11) | 0.0325 (14) | 0.0197 (12) | 0.0018 (10) | 0.0024 (9) | 0.0009 (10) |
| C2                                  | 0.0166 (11) | 0.0283 (13) | 0.0177 (12) | −0.0059 (9) | 0.0005 (9) | 0.0007 (10) |
| C3                                  | 0.0266 (12) | 0.0168 (12) | 0.0188 (12) | −0.0022 (9) | 0.0024 (9) | −0.0011 (9) |
| C4                                  | 0.0277 (13) | 0.0170 (12) | 0.0217 (13) | 0.0032 (10) | 0.0010 (10) | 0.0013 (9) |
| C5                                  | 0.0200 (12) | 0.0231 (13) | 0.0204 (12) | 0.0055 (9) | 0.0002 (9) | 0.0006 (10) |
| C6                                  | 0.0160 (11) | 0.0284 (14) | 0.0196 (12) | −0.0039 (9) | 0.0012 (9) | 0.0019 (10) |
| C7                                  | 0.0220 (12) | 0.0247 (13) | 0.0180 (12) | −0.0079 (10) | 0.0019 (9) | 0.0005 (10) |
| O1                                  | 0.0139 (8) | 0.0326 (10) | 0.0264 (9) | −0.0032 (7) | 0.0042 (7) | −0.0062 (8) |
| O2                                  | 0.0180 (8) | 0.0205 (9) | 0.0344 (10) | 0.0007 (7) | 0.0064 (7) | −0.0047 (7) |
| O3                                  | 0.0163 (8) | 0.0221 (9) | 0.0213 (9) | −0.0015 (6) | 0.0027 (6) | 0.0006 (7) |
| O4                                  | 0.0141 (8) | 0.0318 (10) | 0.0189 (8) | 0.0030 (7) | 0.0029 (6) | −0.0025 (7) |
| C8                                  | 0.0160 (11) | 0.0201 (12) | 0.0115 (11) | −0.0006 (9) | 0.0004 (8) | 0.0027 (9) |
| C9                                  | 0.0196 (12) | 0.0212 (12) | 0.0177 (12) | −0.0045 (9) | −0.0005 (9) | 0.0014 (9) |
| C10                                 | 0.0253 (12) | 0.0192 (12) | 0.0210 (12) | 0.0013 (10) | −0.0002 (9) | −0.0023 (10) |
| C11                                 | 0.0202 (11) | 0.0234 (13) | 0.0170 (12) | 0.0062 (9) | 0.0021 (9) | −0.0006 (9) |
| C12                                 | 0.0153 (11) | 0.0240 (12) | 0.0103 (10) | 0.0017 (9) | 0.0000 (8) | 0.0026 (9) |
| C13                                 | 0.0189 (11) | 0.0151 (11) | 0.0132 (11) | 0.0006 (9) | 0.0013 (8) | 0.0009 (9) |
| C14                                 | 0.0180 (11) | 0.0201 (12) | 0.0134 (11) | 0.0002 (9) | 0.0031 (8) | 0.0024 (9) |
| C15                                 | 0.0162 (11) | 0.0267 (13) | 0.0085 (10) | 0.0019 (9) | 0.0010 (8) | 0.0007 (9) |
| O2W                                 | 0.0220 (9) | 0.0260 (9) | 0.0201 (9) | −0.0036 (7) | 0.0021 (7) | 0.0005 (7) |
### Geometric parameters (Å, °)

|       | Cu1—N1   | Cu1—N2   | Cu1—N3   | Cu1—N4   | Cu1—O1W  | Cu1—O2W  | O1W—H1WB | O1W—H1WA | N1—H1B  | N1—H1A  | N1—C1    | N2—H2    | N2—C2    | N2—C3    | N3—H3    | N3—C5    | N3—C6    | N4—H4B   | N4—H4A   | N4—C7    | C1—H1C   | C1—H1D   | C1—C2    | C2—H2A   | C2—H2B   | C3—H3A   | C3—H3B   | C3—C4    | C4—H4C   | O1W—Cu1—O2W | N1—Cu1—O1W | N1—Cu1—N2 | N1—Cu1—N3 | N1—Cu1—O2W | N2—Cu1—O1W | N2—Cu1—N3 | N2—Cu1—O2W | N3—Cu1—O1W | N3—Cu1—O2W | N4—Cu1—O1W | N4—Cu1—N1 | N4—Cu1—N2 | N4—Cu1—N3   |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|       | 2.0203 (18) | 2.0218 (18) | 2.0279 (18) | 2.0064 (19) | 2.3800 (16) | 2.6562 (16) | 0.8700 | 0.8698 | 0.9699 | 0.9701 | 1.488 (3) | 0.9798 | 1.485 (3) | 1.480 (3) | 0.9799 | 1.486 (3) | 1.486 (3) | 0.9900 | 1.485 (3) | 0.9900 | 1.506 (3) | 0.9900 | 0.9900 | 0.9900 | 0.9900 | 1.529 (3) | 0.9900 | 174.64 (6) | 93.38 (7) | 85.64 (8) | 174.88 (8) | 86.75 (6) | 94.42 (7) | 92.97 (7) | 90.93 (6) | 91.63 (7) | 88.35 (6) | 89.86 (7) | 95.19 (8) | 175.59 (7) | 85.83 (8) |
|       | C4—H4D   | C4—C5    | C5—H5A   | C5—H5B   | C6—H6A   | C6—H6B   | C6—C7   | C7—H7A   | C7—H7B   | C14—O1   | C14—O2   | C15—O3   | C15—O4   | C8—C9    | C8—C13   | C9—C10   | C9—H9    | O2W—H2WA | O2W—H2WB | O3W—H3WA | O3W—H3WB | 174.64 (6) | 93.38 (7) | 85.64 (8) | 174.88 (8) | 86.75 (6) | 94.42 (7) | 92.97 (7) | 90.93 (6) | 91.63 (7) | 88.35 (6) | 89.86 (7) | 95.19 (8) | 175.59 (7) | 85.83 (8) |
|       | 0.9900   | 1.526 (3) | 0.9900   | 0.9900   | 0.9900   | 0.9900   | 1.514 (3) | 0.9900   | 0.9900   | 1.256 (3) | 1.261 (3) | 1.258 (3) | 1.271 (3) | 1.390 (3) | 1.399 (3) | 1.393 (3) | 0.9500   | 0.8698   | 0.8699   | 0.8699   | 112.24 (19) | 107.9   | 109.2   | 109.2   | 108.6   | 108.6   | 107.6   | 114.52 (19) | 108.6   | 108.6   | 111.29 (19) | 109.4   | 109.4   | 109.4   |
N4—Cu1—O2W  84.80 (6)  C4—C5—H5B  109.4
Cu1—O1W—H1WB  123.5  H5A—C5—H5B  108.0
Cu1—O1W—H1WA  127.1  N3—C6—H6A  109.9
H1WB—O1W—H1WA  109.1  N3—C6—H6B  109.9
Cu1—N1—H1B  109.8  N3—C6—C7  108.80 (18)
Cu1—N1—H1A  112.6  H6A—C6—H6B  108.3
H1B—N1—H1A  105.8  C7—C6—H6A  109.9
C1—N1—Cu1  108.02 (14)  C7—C6—H6B  109.9
C1—N1—H1B  110.1  N4—C7—C6  107.68 (18)
C1—N1—H1A  110.5  N4—C7—H7A  110.2
Cu1—N2—H2  109.8  N4—C7—H7B  110.2
C2—N2—Cu1  107.27 (14)  C6—C7—H7A  110.2
C2—N2—H2  106.6  C6—C7—H7B  110.2
C3—N2—Cu1  115.92 (14)  H7A—C7—H7B  108.5
C3—N2—H2  104.7  C9—C8—C13  119.4 (2)
C3—N2—C2  112.19 (18)  C9—C8—C14  120.8 (2)
Cu1—N3—H3  107.9  C13—C8—C14  119.8 (2)
C5—N3—Cu1  115.52 (14)  C8—C9—H9  119.9
C5—N3—H3  105.4  C8—C9—C10  120.3 (2)
C5—N3—C6  112.04 (18)  C10—C9—H9  119.9
C6—N3—Cu1  107.10 (14)  C9—C10—H10  120.0
C6—N3—H3  108.6  C10—C11—H11  119.6
Cu1—N4—H4B  115.0  C10—C11—C12  120.0 (2)
Cu1—N4—H4A  107.8  C10—C11—C12  120.0 (2)
H4B—N4—H4A  109.8  C11—C12—C13  119.7 (2)
C7—N4—Cu1  108.08 (14)  C11—C12—C14  120.3 (2)
C7—N4—H4B  109.8  C11—C12—C15  120.7 (2)
C7—N4—H4A  105.9  C12—C13—C8  119.7
N1—C1—H1C  111.1  C12—C13—C15  120.3 (2)
N1—C1—H1D  111.1  C8—C13—H13  119.7
N1—C1—H1C  107.93 (18)  C12—C13—C14  120.7 (2)
H1C—C1—H1D  108.4  C12—C13—C15  119.7 (2)
C2—C1—H1C  110.1  C12—C13—C14  125.0 (2)
C2—C1—H1D  110.1  O1—C14—O2  117.7 (2)
N2—C2—C1  109.08 (18)  O2—C14—C8  117.24 (19)
N2—C2—H2A  109.9  O3—C15—O4  124.6 (2)
N2—C2—H2B  109.9  O3—C15—C12  118.88 (19)
C1—C2—H2A  109.9  O4—C15—C12  116.5 (2)
C1—C2—H2B  109.9  Cu1—O2W—H2WA  115.4
H2A—C2—H2B  108.3  Cu1—O2W—H2WB  121.9
N2—C3—H3A  109.2  H2WA—O2W—H2WB  108.9
N2—C3—H3B  109.2  H3WA—O3W—H3WB  106.0
Cu1—N1—C1—C2 −38.5 (2)  C9—C8—C14—O1 −9.2 (3)
Cu1—N2—C2—C1 −39.5 (2)  C9—C8—C14—O2  172.7 (2)
Cu1—N2—C3—C4  58.8 (2)  C9—C10—C11—C12  0.1 (3)
Cu1—N3—C5—C4 −60.6 (2)  C10—C11—C12—C13  0.2 (3)
Cu1—N3—C6—C7  38.7 (2)  C10—C11—C12—C15  179.8 (2)
Cu1—N4—C7—C6 39.9 (2)  C11—C12—C13—C8  −0.3 (3)
N1—C1—C2—N2  52.4 (2)  C11—C12—C15—O3  169.8 (2)
N2—C3—C4—C5  −67.6 (3)  C11—C12—C15—O4  −10.7 (3)
N3—C6—C7—N4  −52.8 (2)  C13—C8—C9—C10  0.2 (3)
C2—N2—C3—C4  −177.47 (18)  C13—C8—C14—O1  169.8 (2)
C3—N2—C2—C1  167.89 (18)  C13—C8—C14—O2  −8.3 (3)
C3—C4—C5—N3  68.4 (3)  C13—C12—C15—O3  −10.6 (3)
C5—N3—C6—C7  166.35 (18)  C13—C12—C15—O4  168.89 (19)
C6—N3—C5—C4  176.36 (18)  C14—C8—C9—C10  179.2 (2)
C8—C9—C10—C11  −0.3 (3)  C14—C8—C13—C12  −178.94 (19)
C9—C8—C13—C12  0.1 (3)  C15—C12—C13—C8  −179.90 (19)

Hydrogen-bond geometry (Å, °)

| D—H···A      | D—H  | H···A | D···A     | D—H···A |
|--------------|------|------|-----------|---------|
| N1—H1A···O2W | 0.97 | 2.30 | 3.143 (2) | 145     |
| N1—H1B···O3ui| 0.97 | 2.07 | 3.007 (2) | 161     |
| N2—H2···O4ui | 0.98 | 1.95 | 2.907 (2) | 163     |
| N3—H3···O1   | 0.98 | 2.19 | 3.063 (3) | 148     |
| N4—H4A···O3Wv| 0.97 | 2.10 | 3.042 (2) | 163     |
| N4—H4B···O3v | 0.97 | 2.17 | 3.054 (2) | 151     |
| O1W···H1A···O1vi | 0.87 | 1.89 | 2.747 (2) | 169     |
| O1W···H1B···O4ui| 0.87 | 1.89 | 2.760 (2) | 174     |
| O2W···H2A···O3ui| 0.87 | 2.09 | 2.930 (2) | 161     |
| O2W···H2B···O3W | 0.87 | 2.00 | 2.872 (2) | 175     |
| O3W···H3A···O2ui| 0.87 | 2.00 | 2.823 (2) | 157     |
| O3W···H3B···O2  | 0.87 | 1.85 | 2.712 (2) | 174     |

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