Synthesis, crystal structure and photophysical properties of chlorido[(E)-3-hydroxy-2-methyl-6-(quinolin-8-yl diazenyl)phenolato]copper(II) monohydrate

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The reaction between copper(II) chloride dihydrate and the (E)-2-methyl-4-(quinolin-8-yl diazenyl)benzene-1,3-diol ligand in acetonitrile leads to the formation of the title compound, [Cu(C_{16}H_{12}N_{3}O_{2})Cl].H_{2}O. The ligand is deprotonated and coordinates with three donor atoms (tridentate) to the Cu^{II} ion. Individual molecules of the Cu^{II} complex are connected by chloride bridges, forming a one-dimensional coordination polymer. No photoisomerization to the cis isomer of the azo ligand was observed upon irradiation with UV light.

1. Chemical context

Azobenzene derivatives are well-known dyes with fascinating characteristics such as cis–trans photoisomerization and azo–hydrazone tautomerism. The combination of azo compounds with metal ions to form complexes is a promising approach for controlling their photophysical properties. In metal complexes with azo ligands, the metal centers and azo ligands can affect each other’s properties. For example, cis–trans photoisomerization by irradiation with a single frequency of light has been achieved in azo-conjugated metal complexes by a combination of the photophysical and the redox properties of ligand and metal center (Nishihara, 2005). Azobenzene derivatives with hydroxy groups in the ortho or para position tend to form hydrazone tautomers (Jacques et al., 1979; Ball & Nicholls, 1982; Rauf et al., 2015). A hydrazone tautomer can be converted to an azo tautomer by complexation to the metal ion (Chen et al., 2012; Cai et al., 2016). In this study, we used the ortho and para isomer of the hydroxy-substituted azo-benzene derivative, (E)-2-methyl-4-(quinolin-8-yl diazenyl)benzene-1,3-diol, to investigate azo–hydrazone tautomerism in its Cu^{II} complex. The photophysical properties of the ligand and the Cu^{II} complex were studied by UV–Vis spectroscopy to address the potential photoisomerization.
2. Structural commentary

The crystal structure of the Cu II complex is shown in Fig. 1. The asymmetric unit contains one Cu II complex and one solvent water molecule. The hydroxy group in the ortho-position of the azo ligand is deprotonated and is coordinated to the Cu II center. In the asymmetric unit, the Cu II ion is 4-coordinated in a distorted square-planar geometry. The donor atoms comprise one nitrogen atom of the quinoline moiety, one nitrogen atom of the azo group, one deprotonated alcohol oxygen atom, and a chloride ion. The other hydroxy group of the azo ligand, in the para-position, remains protonated. The chlorido ligand is also weakly coordinated by an adjacent Cu II center occupying its apical position, resulting in an elongated square-pyramidal coordination polyhedron around the copper(II) ions. The Cu1—Cl1i distance in the apical position is 2.7395 (10) Å, which is notably longer than the distances in the equatorial positions, Cu1—Cl1 = 2.2803 (8) Å, Cu1—O1 = 1.917 (2) Å, Cu1—N1 = 2.008 (3) Å, and Cu1—N2 = 1.945 (3) Å [symmetry code: (i) x + 1, y, z]. The N2—N3 bond distance of 1.293 (4) Å is typical for the N=N double bond of an azo group. The structural features of the aromatic rings and the C11—O1 single-bond length of 1.300 (4) Å also indicate that the ligand adopts the azo structure, rather than the hydrazone structure, which is similar to the structures observed in analogous azo-metal complexes with other metals, including Ni, Cu, and Zn (Cai et al., 2016; Kochem et al., 2011, 2014).

3. Supramolecular features

The coordinated chloride ion bridges adjacent Cu II complexes to form a one-dimensional coordination polymer resulting in columns along the crystallographic a-axis direction (Fig. 2). This is supported by π–π stacking between the co-planar quinoline rings with a centroid-centroid distance of 3.7711 (4) Å, an inter-plane distance of 3.3494 (12) Å, and a slippage of 1.733 (2) Å. The 1D columns are linked through hydrogen bonds facilitated by the solvent water molecules, C14—H14—O3, O2—H2A—O3, O3—H3W—Cl1i, and O3—H4W—O1ii, [symmetry codes: (i) x + 1/2, −y + 1/2, z; (ii) x, −y + 1, z − 1/2] (Table 1, Fig. 3).

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.42, update of November 2020; Groom et al., 2016) with

|                  | D—H···A   | D—H   | H···A | D···A   | D—H···A |
|------------------|-----------|-------|-------|---------|---------|
| Cl4—H14···O3    | 0.95      | 2.65  | 3.318 (4) | 128    |
| O2—H2A···O3     | 0.82 (4)  | 1.87 (4) | 2.686 (4) | 172 (4) |
| O3—H3W···Cl1i   | 0.70 (4)  | 2.45 (4) | 3.104 (3) | 157 (5) |
| O3—H4W···O1ii   | 0.89 (6)  | 2.20 (6) | 2.911 (4) | 136 (4) |

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

Figure 1
Crystal structure of the title compound showing the atom-labeling scheme, generated with Mercury software (Version 2021.2.0; Macrae et al., 2020). Displacement ellipsoids are drawn at the 50% probability level.

Figure 2
Crystal packing of the title compound viewed along the b axis showing intermolecular hydrogen bonds and π–π stacking between the azo ligands, generated with Mercury software (Version 2021.2.0; Macrae et al., 2020). Intermolecular hydrogen bonds are shown as blue dashed lines.
ConQuest (Version 2020.3.0; Bruno et al., 2002) for phenyl- and quinolinyl-bearing azo ligands with an ortho-hydroxy substituent and their complexes resulted in only seven hits. These structures include one ligand derivative and six transition-metal complexes (an azobenzene derivative and its Zn complex, refcodes ONOKUY and ONOLAF; Kochem et al., 2011; Cu complexes, refcodes MOGLAX and MOGLEB; Kochem et al., 2014; an Re complex, refcode TOZTUZ; Sarkar et al., 2015; a Co complex, refcode VARQUD; Taylor et al., 2017; an Ho complex, refcode NAMJIY; Taylor et al., 2018). While co-planarity of the aromatic moieties was observed in some of these structures, the formation of the column-type coordination polymeric structure of the title compound has no precedence in this group.

5. UV–Vis spectra for the azo ligand and CuII complex

The UV–Vis spectra of the azo ligand and the CuII complex in CH3CN are shown in Fig. 4. The maximum of the extinction (εmax) was observed at 406 nm for the ligand, while the CuII complex showed decreased absorption and red-shifted maxima at 420 and 489 nm. To investigate the photo-isomerization of the ligand and the CuII complex, the samples were irradiated at maximum wavelength, but no photo-isomerization to the cis isomer was observed for either compound.

6. Synthesis and crystallization

To synthesize the title ligand, an aqueous solution of 1.2 M NaNO2 (3 mL) was slowly added to a cold solution of 8-aminooquinoline (0.432 g, 3.00 mmol) in 0.5 M HCl(aq) (20 mL). The resulting solution was stirred at 277 K for 15 min, and an aqueous solution of (NH2)2CO (0.180 g, 3.00 mmol) in 3 mL of water was then added to give a diazonium chloride solution. This solution was added to an aqueous 0.25 M NaOH solution of 2,6-dihydroxytoluene (0.372 g, 3.00 mmol) and stirred at 277 K for 30 min and then stirred at room temperature for 15 h. The reaction mixture was acidified with 1 M HCl(aq) (10 mL) and a red precipitate was formed. The precipitate was filtered off and washed with water and then with cold tetrahydrofuran. Yield, 86% (0.787 g, 2.58 mmol). IR: νmax (KBr): 3400, 3068, 1633, 1536, 1503, 1488, 1447, 1364, 1299, 1212, 787 cm⁻¹. ¹H NMR (400 MHz, CD3CN): δH 9.06 (d, 1H), 8.41 (d, 1H), 8.20 (d, 1H), 7.97 (d, 1H), 7.74 (t, 1H), 7.62 (dd, 1H), 7.49 (d, 1H), 6.63 (d, 1H), 2.12 (s, 3H). Analysis calculated for C16H13N3O2·0.72HCl: C, 62.90; H, 4.53; N, 13.75. Found: C, 62.49; H, 4.31; N, 14.17. The CuII complex was obtained as a brown solid by the reaction of the azo ligand synthesized as described above (0.099 g, 0.324 mmol) in 4 mL of ethanol with CuCl2·2H2O (0.061 g, 0.358 mmol) in 2 mL of H2O. Yield,

Table 2

| Crystal data | Chemical formula: [Cu(C16H12N3O2)Cl]·H2O |
|--------------|--------------------------------------|
| Mₚ          | 395.29                               |
| Crystal system, space group | Monoclinic, P2₁/n |
| Temperature (K) | 100                                 |
| a, b, c (Å) | 3.7711 (4), 26.451 (3), 15.0864 (15) |
| β (°)       | 97.100 (2)                           |
| γ (Å)       | 1495.3 (3)                           |
| Z           | 4                                     |
| Radiation type | Mo Kα                             |
| μ (mm⁻¹)    | 1.66                                  |
| Crystal size (mm) | 0.44 × 0.09 × 0.02                  |

Data collection

| Diffractometer | Bruker APEX2 CCD                        |
|----------------|----------------------------------------|
| Absorption correction | Multi-scan (SADABS; Krause et al., 2015) |
| Tmin, Tmax | 0.629, 0.745                           |
| No. of measured, independent and observed | 8133, 2746, 2132 |
| Rint (sin θ/λ)max (Å⁻¹) | 0.049                                  |
| Reﬁnement |
| R[F² > 2σ(F²)], wR(F²), S | 0.036, 0.081, 1.04 |
| No. of reﬂections | 2746                                    |
| No. of parameters | 230                                     |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.42, −0.41 |

Computer programs: APEX2 and SAINT (Bruker, 2014), SHELXTL2014/5 (Sheldrick, 2015a), SHELXL2017/7 (Sheldrick, 2015b), and SHELXTL (Sheldrick, 2008).

Figure 3

Crystal packing of the title compound viewed along the a axis showing intermolecular hydrogen bonds (blue dashed lines), generated with Mercury software (Version 2021.2.0; Macrae et al., 2020).

Figure 4

UV–Vis spectra of the ligand and the title compound in CH3CN.
54% (0.073 g, 0.193 mmol). Crystals of the CuII complex suitable for the X-ray crystallography study were obtained by the slow diffusion of a CH3CN solution of the ligand into an aqueous solution of CuCl2·2H2O. IR: νmax (KBr): 3418, 2924, 2854, 1633, 1557, 1508, 1436, 1283, 1258, 1048 cm⁻¹. Analysis calculated for C16H12ClCuN3O2: C, 50.94; H, 3.21; N, 11.14. Found: C, 50.82; H, 3.63; N, 11.49.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. The O—H hydrogen atoms of the solvent water molecules and the hydroxy group in the para-position were found in the difference-Fourier map and were refined isotropically without restraints or constraints. Other hydrogen atoms were generated geometrically, and refined with a riding model with C—H = 0.98 Å, Uiso(H) = 1.5 Ueq(C) for methyl, and C—H = 0.95 Å, Uiso(H) = 1.2 Ueq(C) for aromatic hydrogen atoms. Two reflections were omitted as clear outliers.

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Synthesis, crystal structure and photophysical properties of chlorido[(E)-3-hydroxy-2-methyl-6-(quinolin-8-yldiazenyl)phenolato]copper(II) monohydrate

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Computing details

Data collection: APEX2 (Bruker, 2014); cell refinement: SAINT (Bruker, 2014); data reduction: SAINT (Bruker, 2014); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2017/1 (Sheldrick, 2015b); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Chlorido[(E)-3-hydroxy-2-methyl-6-(quinolin-8-yldiazenyl)phenolato]copper(II) monohydrate

Crystal data

[Cu(C_{16}H_{12}N_{3}O_{2})Cl]·H_{2}O

$M_f = 395.29$

Monoclinic, $P2_1/n$

$a = 3.7711$ (4) Å

$b = 26.451$ (3) Å

$c = 15.0864$ (15) Å

$\beta = 97.100$ (2)$^\circ$

$V = 1493.3$ (3) Å$^3$

$Z = 4$

$F(000) = 804$

$D_\lambda = 1.758$ Mg m$^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1510 reflections

$\theta = 2.7$–24.3$^\circ$

$\mu = 1.66$ mm$^{-1}$

$T = 100$ K

Plate, brown

0.44 x 0.09 x 0.02 mm

Data collection

Bruker APEXII CCD
diffractometer

$\phi$ and $\omega$ scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

$T_{\text{min}} = 0.629$, $T_{\text{max}} = 0.745$

8133 measured reflections

2746 independent reflections

2132 reflections with $I > 2\sigma(I)$

$R_{int} = 0.049$

$\theta_{\text{max}} = 25.4^\circ$, $\theta_{\text{min}} = 2.1^\circ$

$h = -4\rightarrow 4$

$k = -21\rightarrow 31$

$l = -17\rightarrow 18$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.081$

$S = 1.04$

2746 reflections

230 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_c^2) + (0.0286P)^2 + 0.6665P]$

where $P = (F_c^2 + 2F_s^2)/3$

$\Delta\sigma_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.42$ e Å$^{-3}$

$\Delta\rho_{\text{min}} = -0.41$ e Å$^{-3}$
**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 (Å²)**

|    | x     | y     | z     | U(eq) |
|----|-------|-------|-------|-------|
| C1 | 0.9143 (9) | 1.03984 (12) | 0.8827 (2) | 0.0157 (7) |
| H1 | 0.822246 | 1.026099 | 0.933371 | 0.019* |
| C2 | 0.9909 (9) | 1.09143 (12) | 0.8821 (2) | 0.0162 (7) |
| H2 | 0.951775 | 1.111932 | 0.931701 | 0.019* |
| C3 | 1.1222 (9) | 1.11240 (12) | 0.8101 (2) | 0.0176 (8) |
| H3 | 1.174056 | 1.147528 | 0.809169 | 0.021* |
| C4 | 1.1803 (9) | 1.08129 (12) | 0.7369 (2) | 0.0146 (7) |
| C5 | 1.3129 (9) | 1.09847 (12) | 0.6585 (2) | 0.0156 (8) |
| H5 | 1.371662 | 1.133133 | 0.652668 | 0.019* |
| C6 | 1.3564 (8) | 1.06562 (12) | 0.5914 (2) | 0.0154 (7) |
| H6 | 1.440700 | 1.077948 | 0.538699 | 0.018* |
| C7 | 1.2798 (8) | 1.01391 (12) | 0.5981 (2) | 0.0140 (7) |
| H7 | 1.314425 | 0.991581 | 0.550631 | 0.017* |
| C8 | 1.1548 (8) | 0.99580 (12) | 0.6736 (2) | 0.0124 (7) |
| C9 | 1.0988 (8) | 1.02935 (12) | 0.7434 (2) | 0.0127 (7) |
| C10 | 1.0113 (9) | 0.86492 (12) | 0.6316 (2) | 0.0140 (7) |
| C11 | 0.8938 (8) | 0.83965 (12) | 0.7082 (2) | 0.0132 (7) |
| C12 | 0.8113 (9) | 0.78725 (12) | 0.7008 (2) | 0.0151 (7) |
| C13 | 0.8379 (9) | 0.76272 (12) | 0.6209 (2) | 0.0164 (8) |
| C14 | 0.9591 (9) | 0.78717 (13) | 0.5468 (2) | 0.0184 (8) |
| H14 | 0.979522 | 0.768954 | 0.493360 | 0.022* |
| C15 | 1.0453 (9) | 0.83666 (12) | 0.5529 (2) | 0.0160 (7) |
| H15 | 1.130421 | 0.852982 | 0.503555 | 0.019* |
| C16 | 0.6924 (9) | 0.75947 (12) | 0.7792 (2) | 0.0180 (8) |
| H16A | 0.534473 | 0.731513 | 0.757445 | 0.027* |
| H16B | 0.563395 | 0.782752 | 0.814287 | 0.027* |
| H16C | 0.901857 | 0.746056 | 0.816731 | 0.027* |
| C11 | 0.5361 (2) | 0.92919 (3) | 0.91540 (5) | 0.0160 (2) |
| Cu1 | 0.90089 (11) | 0.93390 (2) | 0.80589 (2) | 0.01287 (13) |
| H2A | 0.747 (11) | 0.7051 (16) | 0.563 (3) | 0.045 (14)* |
| H3W | 0.853 (12) | 0.6570 (17) | 0.448 (3) | 0.043 (18)* |
| H4W | 0.533 (15) | 0.674 (2) | 0.412 (4) | 0.09 (2)* |
| N1 | 0.9636 (7) | 1.00915 (10) | 0.81610 (16) | 0.0126 (6) |
| N2 | 1.0654 (7) | 0.94509 (10) | 0.69027 (17) | 0.0141 (6) |
| N3 | 1.0982 (7) | 0.91430 (10) | 0.62523 (17) | 0.0131 (6) |
| O1 | 0.8645 (6) | 0.86267 (8) | 0.78313 (14) | 0.0157 (5) |
| O2 | 0.7473 (7) | 0.71334 (9) | 0.61565 (17) | 0.0225 (6) |
| O3 | 0.7360 (10) | 0.67746 (11) | 0.44880 (19) | 0.0275 (7) |
** Atomic displacement parameters (Å²)**

|        | U¹¹     | U¹²     | U¹³     | U²²     | U²³     | U³³     |
|--------|---------|---------|---------|---------|---------|---------|
| C1     | 0.0175 (19) | 0.0184 (18) | 0.0110 (16) | 0.0034 (15) | 0.0011 (14) | 0.0007 (15) |
| C2     | 0.0185 (19) | 0.0147 (18) | 0.0144 (17) | 0.0026 (15) | −0.0016 (15) | −0.0033 (15) |
| C3     | 0.023 (2) | 0.0077 (17) | 0.0206 (18) | 0.0023 (14) | −0.0033 (15) | −0.0017 (15) |
| C4     | 0.0135 (18) | 0.0114 (17) | 0.0180 (17) | 0.0024 (14) | −0.0012 (15) | 0.0000 (14) |
| C5     | 0.0162 (19) | 0.0076 (17) | 0.0223 (19) | −0.0023 (14) | −0.0001 (15) | 0.0044 (15) |
| C6     | 0.0148 (18) | 0.0175 (18) | 0.0136 (16) | −0.0015 (15) | 0.0006 (14) | 0.0045 (15) |
| C7     | 0.0126 (17) | 0.0162 (18) | 0.0136 (16) | 0.0003 (14) | 0.0029 (14) | −0.0019 (15) |
| C8     | 0.0114 (17) | 0.0126 (17) | 0.0131 (16) | 0.0020 (14) | 0.0004 (13) | 0.0018 (14) |
| C9     | 0.0106 (17) | 0.0144 (18) | 0.0122 (16) | 0.0017 (13) | −0.0027 (14) | −0.0006 (14) |
| C10    | 0.0137 (18) | 0.0123 (17) | 0.0160 (17) | 0.0007 (14) | 0.0010 (14) | −0.0014 (14) |
| C11    | 0.0107 (17) | 0.0137 (17) | 0.0145 (16) | 0.0017 (14) | −0.0011 (14) | 0.0000 (14) |
| C12    | 0.0168 (19) | 0.0120 (17) | 0.0168 (17) | −0.0014 (14) | 0.0029 (14) | −0.0002 (15) |
| C13    | 0.020 (2) | 0.0086 (17) | 0.0205 (18) | 0.0002 (14) | 0.0003 (15) | −0.0002 (15) |
| C14    | 0.025 (2) | 0.0156 (18) | 0.0142 (17) | 0.0045 (15) | 0.0025 (15) | −0.0033 (15) |
| C15    | 0.0218 (19) | 0.0124 (18) | 0.0142 (16) | −0.0021 (15) | 0.0043 (15) | −0.0009 (15) |
| C16    | 0.022 (2) | 0.0126 (17) | 0.0196 (18) | −0.0015 (15) | 0.0036 (16) | −0.0004 (15) |
| Cl1    | 0.0190 (4) | 0.0161 (4) | 0.0137 (4) | 0.0011 (4) | 0.0049 (3) | 0.0009 (3) |
| Cu1    | 0.0193 (2) | 0.0089 (2) | 0.0110 (2) | −0.00015 (17) | 0.00432 (16) | −0.00005 (17) |
| N1     | 0.0161 (15) | 0.0102 (14) | 0.0112 (13) | 0.0040 (12) | 0.0011 (12) | −0.0001 (12) |
| N2     | 0.0178 (16) | 0.0110 (14) | 0.0141 (14) | −0.0007 (12) | 0.0046 (12) | 0.0001 (12) |
| N3     | 0.0165 (16) | 0.0110 (14) | 0.0115 (14) | −0.0005 (12) | 0.0004 (12) | −0.0012 (12) |
| O1     | 0.0262 (14) | 0.0087 (11) | 0.0130 (11) | −0.0012 (10) | 0.0051 (10) | −0.0013 (10) |
| O2     | 0.0403 (17) | 0.0093 (13) | 0.0195 (14) | −0.0043 (11) | 0.0095 (12) | −0.0056 (11) |
| O3     | 0.040 (2) | 0.0172 (15) | 0.0252 (15) | −0.0017 (15) | 0.0047 (15) | −0.0014 (13) |

** Geometric parameters (Å, °)**

|        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|
| C1—N1  | 1.323 (4) | C11—O1  | 1.300 (4) |
| C1—C2  | 1.395 (5) | C11—C12 | 1.422 (4) |
| C1—H1  | 0.9500  | C12—C13 | 1.383 (4) |
| C2—C3  | 1.366 (4) | C12—C16 | 1.506 (4) |
| C2—H2  | 0.9500  | C13—O2  | 1.350 (4) |
| C3—C4  | 1.416 (4) | C13—C14 | 1.417 (4) |
| C3—H3  | 0.9500  | C14—C15 | 1.349 (4) |
| C4—C9  | 1.414 (4) | C14—H14 | 0.9500  |
| C4—C5  | 1.415 (4) | C15—H15 | 0.9500  |
| C5—C6  | 1.359 (4) | C16—H16A | 0.9800 |
| C5—H5  | 0.9500  | C16—H16B | 0.9800 |
| C6—C7  | 1.404 (4) | C16—H16C | 0.9800 |
| C6—H6  | 0.9500  | C1I—Cu1  | 2.2803 (8) |
| C7—C8  | 1.372 (4) | C1I—Cu1i | 2.7395 (10) |
| C7—H7  | 0.9500  | Cu1—O1  | 1.917 (2) |
| C8—C9  | 1.412 (4) | Cu1—N2  | 1.945 (2) |
| C8—N2  | 1.413 (4) | Cu1—N1  | 2.008 (3) |
| C9—N1  | 1.374 (4) | N2—N3  | 1.293 (3) |
C10—N3 1.353 (4)  O2—H2A 0.82 (4) 
C10—C15 1.423 (4)  O3—H3W 0.70 (4) 
C10—C11 1.451 (4)  O3—H4W 0.89 (6) 

N1—C1—C2 123.2 (3)  O2—C13—C12 117.4 (3) 
N1—C1—H1 118.4  O2—C13—C14 119.9 (3) 
C2—C1—H1 118.4  C12—C13—C14 122.6 (3) 
C3—C2—C1 119.9 (3)  C15—C14—C13 119.2 (3) 
C3—C2—H2 120.1  C15—C14—H14 120.4 
C1—C2—H2 120.1  C13—C14—H14 120.4 
C2—C3—C4 119.4 (3)  C14—C15—C10 121.4 (3) 
C2—C3—H3 120.3  C14—C15—H15 119.3 
C4—C3—H3 120.3  C10—C15—H15 119.3 
C9—C4—C5 118.2 (3)  C12—C16—H16A 109.5 
C9—C4—C3 117.0 (3)  C12—C16—H16B 109.5 
C5—C4—C3 124.8 (3)  H16A—C16—H16B 109.5 
C6—C5—C4 120.3 (3)  C12—C16—H16C 109.5 
C6—C5—H5 119.8  H16A—C16—H16C 109.5 
C4—C5—H5 119.8  H16B—C16—H16C 109.5 
C5—C6—C7 121.6 (3)  Cu1—Cl1—Cu1i 96.97 (3) 
C5—C6—H6 119.2  O1—Cu1—N2 90.72 (10) 
C7—C6—H6 119.2  O1—Cu1—N1 173.25 (9) 
C8—C7—C6 119.7 (3)  N2—Cu1—N1 82.56 (10) 
C8—C7—H7 120.2  O1—Cu1—Cl1 92.28 (6) 
C6—C7—H7 120.2  N2—Cu1—Cl1 161.09 (9) 
C7—C8—C9 119.9 (3)  N1—Cu1—Cl1 94.27 (7) 
C7—C8—N2 126.4 (3)  O1—Cu1—Cl1ii 95.81 (7) 
C8—C9—N2 113.8 (3)  N2—Cu1—Cl1ii 101.29 (8) 
N1—C9—C8 117.1 (3)  N1—Cu1—Cl1ii 85.00 (8) 
N1—C9—C4 122.6 (3)  Cl1—Cu1—Cl1ii 96.97 (3) 
C8—C9—C4 120.3 (3)  C1—N1—Cu1 129.8 (2) 
N3—C10—C15 113.6 (3)  C9—N1—Cu1 112.1 (2) 
N3—C10—C11 127.0 (3)  C11—N1—Cu1 114.6 (2) 
C15—C10—C11 119.4 (3)  N3—N2—C8 114.6 (2) 
O1—C11—C12 118.9 (3)  N3—N2—Cu1 131.0 (2) 
O1—C11—C10 122.9 (3)  C8—N2—Cu1 114.40 (19) 
C12—C11—C10 118.2 (3)  N2—N3—C10 120.5 (3) 
C13—C12—C11 119.1 (3)  C11—O1—Cu1 127.15 (19) 
C13—C12—C16 121.0 (3)  C13—O2—H2A 107 (3) 
C11—C12—C16 119.8 (3)  H3W—O3—H4W 114 (5) 

Symmetry codes: (i) x−1, y, z; (ii) x+1, y, z.

Hydrogen-bond geometry (Å, °)

| D—H—A          | D—H | H···A  | D···A  | D—H···A |
|-----------------|-----|--------|--------|----------|
| C14—H14···O3    | 0.95| 2.65   | 3.318 (4) | 128       |
| O2—H2A···O3     | 0.82 (4) | 1.87 (4) | 2.686 (4) | 172 (4)  |

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|           |        |        |        |        |
|-----------|--------|--------|--------|--------|
| O3—H3W···Cl1\textsuperscript{iii} | 0.70 (4) | 2.45 (4) | 3.104 (3) | 157 (5) |
| O3—H4W···O1\textsuperscript{iv} | 0.89 (6) | 2.20 (6) | 2.911 (4) | 136 (4) |

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