

Synthesis, structure and Hirshfeld surface analysis of diaquadinitratobis(4-nitroaniline)copper(II)

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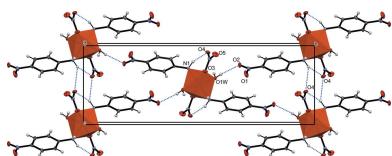
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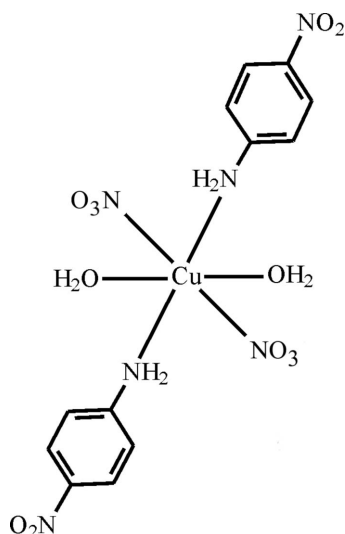
A new metal complex, $[\text{Cu}(\text{NO}_3)_2(\text{C}_6\text{H}_4\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$, was synthesized from water–ethanol solutions of $\text{Cu}(\text{NO}_3)_2$ and 4-nitroaniline (PNA). The complex molecules are located on inversion centers in monoclinic crystals with space group $P2_1/c$. The copper(II) ions are monodentately coordinated by two neutral PNA molecules through the nitrogen atom of the amino group, two NO_3^- anions and two water molecules. The coordination polyhedron of the central ion is a distorted octahedron as a result of the Jahn–Teller effect. There is a weak intramolecular hydrogen bond between the N–H group and the oxygen atom of one nitrate anion. Six relatively weak intermolecular hydrogen bonds associate the complex molecules into a three-dimensional network. The Hirshfeld surface analysis indicates that 55.8% of the intermolecular interactions are from $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts, 13.3% are from $\text{H}\cdots\text{H}$ contacts while other contributions are from $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, $\text{O}\cdots\text{O}$ and other contacts.

1. Chemical context

p-Nitroaniline (PNA) or 1-amino-4-nitrobenzene is an organic compound with the formula $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$. It is a yellow solid and one of three isomers of nitroaniline. PNA is an intermediate in the production of dyes, antioxidants, pharmaceuticals, gasoline, gum inhibitors, poultry medicines, and serves as a corrosion inhibitor. In particular, it is mainly used industrially as a precursor to *p*-phenylenediamine, an important dye component (Booth, 2000). The compound is toxic by way of inhalation, ingestion and absorption and can cause long-term damage to the environment if released as a pollutant. Its LD_{50} is 750.0 mg kg^{-1} when administered orally and therefore it should be handled with great care. It is well known that the biopharmaceutical properties (water solubility, bioavailability and bioactivity) of active pharmaceutical ingredients (API) may be improved by metal complex formation (Khudoyberganov *et al.*, 2022; Ruzmetov *et al.*, 2022*a,b*). Moreover, metal complex formation may be responsible for the reduction of the toxicity of metals, especially in chelation therapy applications and respective investigations (Egorova & Ananikov, 2017; Flora & Pachauri, 2010; Ahmed *et al.*, 2020). At the same time, this technique may similarly lead to a reduction in the toxicity of hazardous organic substances when they are part of coordination compounds. In order to test this hypothesis for specific molecules, we synthesized metal complexes of various toxic organic substances. This article describes the synthesis, molecular and crystal structure and



Hirshfeld surface analysis of the *p*-nitroaniline copper(II) complex.



2. Structural commentary

The molecular structure of the title complex is shown in Fig. 1. The central copper(II) ion is located on a crystallographic inversion center. Each of the two PNA molecules coordinates the metal ion through their NH_2 nitrogen atom. Two NO_3^- groups are attached to the Cu^{2+} ion *via* one of their oxygen atoms (O3) in a monodentate fashion. The other two positions of the octahedral coordination sphere are occupied by water molecules. The formula of the obtained complex is $[\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2(\text{PNA})_2]$. The coordination polyhedron of the central atom is an octahedron with a distortion due to the Jahn–Teller effect. The $\text{Cu1}–\text{O1W}$ and $\text{Cu1}–\text{N1}$ bond lengths are 1.996 (2) and 2.055 (3) Å while the $\text{Cu1}–\text{O3}$ distance is elongated to 2.367 (2) Å based on this effect. Orthogonal bond angles are in the range of 84.01 (11)–95.99 (11)°, *i.e.* their maximum deviation from an ideal value is about 6°. Compensation of the positive charge of the copper

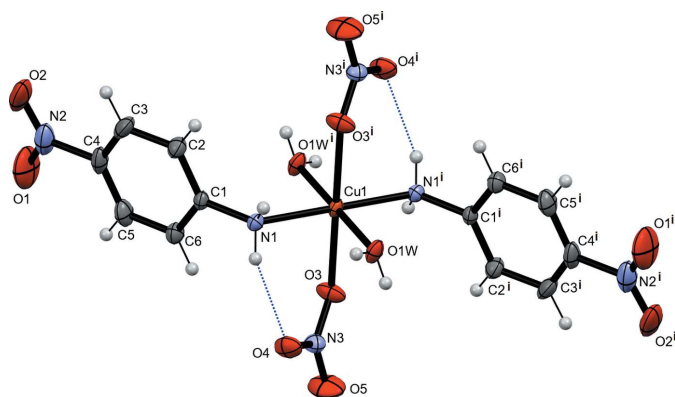


Figure 1

The molecular structure of the PNA copper(II) title complex generated with *Mercury* (Macrae *et al.*, 2020). Displacement ellipsoids are plotted at the 50% probability level. Intramolecular hydrogen bonds between the amine and nitrate groups are shown as dashed lines.

Table 1

Hydrogen-bond geometry (Å, °).

$D–H\cdots A$	$D–H$	$H\cdots A$	$D\cdots A$	$D–H\cdots A$
$\text{N1}–\text{H1A}\cdots\text{O4}$	0.82 (4)	2.30 (4)	3.021 (4)	147 (4)
$\text{O1W}–\text{H1WA}\cdots\text{O3}^{\text{i}}$	0.81 (5)	2.07 (5)	2.828 (4)	156 (5)
$\text{O1W}–\text{H1WA}\cdots\text{O5}^{\text{i}}$	0.81 (5)	2.28 (5)	2.979 (5)	145 (5)
$\text{N1}–\text{H1A}\cdots\text{O4}^{\text{ii}}$	0.82 (4)	2.42 (4)	3.057 (4)	135 (3)
$\text{N1}–\text{H1B}\cdots\text{O3}^{\text{i}}$	0.86 (4)	2.34 (4)	3.103 (4)	148 (4)
$\text{N1}–\text{H1B}\cdots\text{O3}^{\text{iii}}$	0.86 (4)	2.60 (5)	2.968 (4)	107 (3)
$\text{O1W}–\text{H1WB}\cdots\text{O1}^{\text{iv}}$	0.76 (6)	2.64 (5)	3.085 (5)	120 (5)
$\text{O1W}–\text{H1WB}\cdots\text{O2}^{\text{iv}}$	0.77 (6)	2.26 (6)	3.022 (5)	171 (5)

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

ion takes place with the inclusion of the two NO_3^- ions into the inner coordination sphere. The intramolecular $\text{N1}–\text{H}\cdots\text{O4}$ hydrogen bond in the molecule forms a six-membered ring with $S_1^1(6)$ graph-set notation (Etter, 1990). The NO_2 group of PNA is nearly coplanar with the aromatic ring – the corresponding dihedral angle is only 5.8 (6)°.

3. Supramolecular features

There are five proton-acceptor and two proton-donor hydrogen-bonding functional groups in the asymmetric unit of the molecule. All these groups realize their hydrogen-bonding capabilities (Table 1). The respective seven intermolecular hydrogen bonds are relatively weak. A notable feature of the hydrogen-bonding pattern is that a considerable proportion of them are of a bifurcated nature – atoms H1A, H1B and H1WA are simultaneously hydrogen-bonded to two acceptors. The hydrogen bonds form different rings of various dimensions, *i.e.* rings with graph-set notations $R_2^2(4)$, $R_2^1(6)$ and $R_2^2(8)$. The hydrogen bonds summarized in Table 1 connect the complex molecules into a three-dimensional network (Fig. 2). The aromatic moieties are co-planar throughout the crystal lattice but do not engage in $\pi–\pi$ stacking interactions.

The Hirshfeld surfaces were calculated and the two-dimensional fingerprint plots generated using *Crystal-Explorer2021* (Spackman *et al.*, 2021). Fig. 3 shows the three-dimensional Hirshfeld surface of the PNA copper complex with d_{norm} (normalized contact distance) plotted over the range of -0.5385 to 1.2851 a.u. The interactions given in Table 1 play a key role in the molecular packing of the

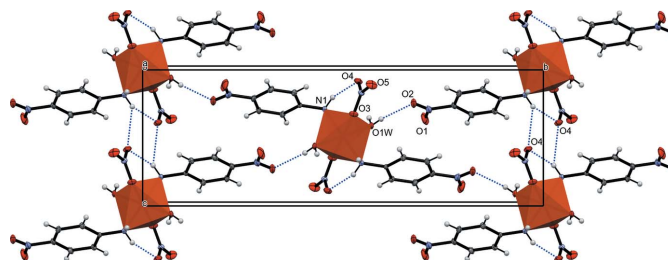


Figure 2

The unit cell of the crystal structure of the title compound with completed molecules viewed along the crystallographic *a* axis of the crystal packing. Hydrogen bonds are shown as dashed lines.

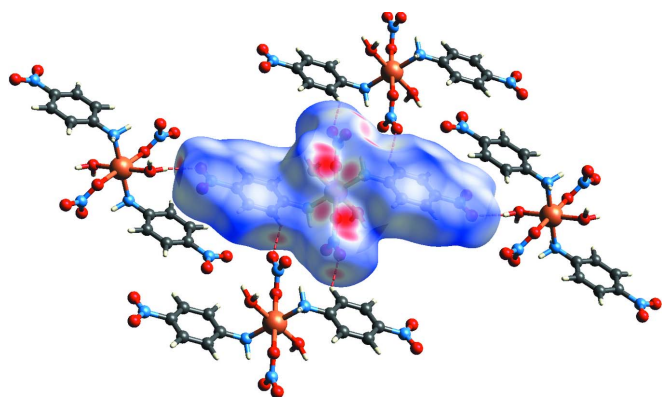


Figure 3
View of the three-dimensional Hirshfeld surface of the PNA copper title complex plotted over d_{norm} .

complex. The overall 2D fingerprint plot and those delineated into the individual contributions are shown in Fig. 4. The percentage contributions to the Hirshfeld surfaces from the various interatomic contacts are as follows: $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ 55.8%, $\text{H}\cdots\text{H}$ 13.3%, $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$ 9.3%, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ 7.7% and $\text{O}\cdots\text{O}$ 6.1%. Other minor contributions to the Hirshfeld surface are from $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ (3.1%), $\text{O}\cdots\text{N}/\text{N}\cdots\text{O}$ (2.2%) and $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ (1.5%) contacts.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, update of November 2021; Groom *et al.*, 2016) for PNA metal complexes gave only five hits. In all entries, neutral PNA molecules are coordinated through their amine nitrogen atoms. In all cases, two chloride ions are coordinated in order to compensate for the twofold positive charge of the central ion. In the structures with refcodes BEMZAW (Feng, 2012), LUKLEK (Nguyen *et al.*, 2015) and MEFWAY (Chen *et al.*, 2017), the coordination polyhedron is tetrahedral while in

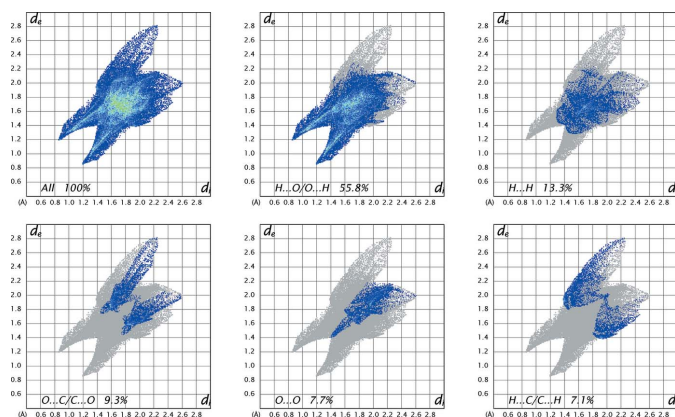


Figure 4
The full two-dimensional fingerprint plots for the PNA copper title complex showing all interactions and delineated into $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ and $\text{O}\cdots\text{O}$ interactions. The d_i and d_e values are the closest internal and external distances (Å) from given points on the Hirshfeld surface.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}(\text{NO}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$
M_r	499.86
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	5.4741 (2), 22.5679 (6), 7.6478 (2)
β (°)	92.286 (3)
V (Å ³)	944.05 (5)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.38
Crystal size (mm)	0.18 × 0.15 × 0.14
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)
$T_{\text{min}}, T_{\text{max}}$	0.829, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8364, 1832, 1457
R_{int}	0.062
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.045, 0.123, 1.04
No. of reflections	1832
No. of parameters	159
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)	0.52, -0.87

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

case of compounds with refcodes HEXBUJ (Ip *et al.*, 2012) and WOJKIR (Belghith *et al.*, 2014), the central ion is sixfold coordinated and the complexes are octahedral. There is no precedent for structures with the coordination of water molecules or NO_3^- anions.

5. Synthesis and crystallization

The salt $\text{Cu}(\text{NO}_3)_2$ (0.187 g, 1.0 mmol) was dissolved in 2 ml of water and 4-nitroaniline (0.276 g, 2 mmol) was dissolved in 2 ml of absolute alcohol at 333 K. The solutions were mixed, filtered and left at room temperature for evaporation. After two weeks, green crystals had formed.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound hydrogen atoms were placed in calculated positions ($\text{C}-\text{H} = 0.93$) and refined in the riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms of the water molecule and the amino group were freely refined.

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2020); cell refinement: *CrysAlis PRO* (Rigaku OD, 2020); data reduction: *CrysAlis PRO* (Rigaku OD, 2020); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Diaquadinitratobis(4-nitroaniline)copper(II)

Crystal data

[Cu(NO₃)₂(C₆H₄N₂O₂)₂(H₂O)₂]

$M_r = 499.86$

Monoclinic, $P2_1/c$

$a = 5.4741$ (2) Å

$b = 22.5679$ (6) Å

$c = 7.6478$ (2) Å

$\beta = 92.286$ (3)°

$V = 944.05$ (5) Å³

$Z = 2$

$F(000) = 510$

$D_x = 1.758$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 2724 reflections

$\theta = 3.9\text{--}70.2^\circ$

$\mu = 2.38$ mm⁻¹

$T = 293$ K

Needle, metallic greenish green

0.18 × 0.15 × 0.14 mm

Data collection

XtaLAB Synergy, Single source at home/near,

HyPix3000

diffractometer

Radiation source: micro-focus sealed X-ray

tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlisPro*; Rigaku OD, 2020)

$T_{\min} = 0.829$, $T_{\max} = 1.000$

8364 measured reflections

1832 independent reflections

1457 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 71.5^\circ$, $\theta_{\min} = 3.9^\circ$

$h = -6 \rightarrow 6$

$k = -27 \rightarrow 19$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.123$

$S = 1.04$

1832 reflections

159 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.7131P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.52 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.87 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2019/2

(Sheldrick 2015a),

$$F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0033 (5)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.500000	0.500000	0.500000	0.0261 (2)
O1W	0.6912 (5)	0.57083 (11)	0.4300 (4)	0.0379 (6)
N1	0.6669 (6)	0.45393 (11)	0.3061 (4)	0.0294 (6)
O3	0.1479 (4)	0.52675 (14)	0.3283 (3)	0.0495 (7)
O4	0.3458 (5)	0.53819 (13)	0.0932 (4)	0.0554 (7)
N3	0.1596 (5)	0.54597 (13)	0.1725 (4)	0.0370 (6)
C1	0.6119 (6)	0.39265 (13)	0.2771 (4)	0.0282 (6)
O2	0.5581 (9)	0.17631 (14)	0.2427 (5)	0.0967 (14)
O5	-0.0187 (6)	0.57134 (19)	0.1086 (5)	0.0865 (12)
C6	0.4005 (6)	0.37830 (15)	0.1797 (5)	0.0379 (8)
H6	0.300983	0.408167	0.132632	0.046*
N2	0.4156 (10)	0.21426 (17)	0.1934 (6)	0.0727 (13)
C2	0.7614 (7)	0.34918 (15)	0.3474 (5)	0.0400 (8)
H2	0.901766	0.358992	0.413589	0.048*
C4	0.4876 (8)	0.27703 (16)	0.2229 (5)	0.0490 (10)
C5	0.3390 (8)	0.32017 (17)	0.1532 (5)	0.0488 (9)
H5	0.197557	0.310181	0.088452	0.059*
C3	0.6984 (9)	0.28969 (16)	0.3173 (6)	0.0532 (11)
H3	0.798430	0.259361	0.360899	0.064*
O1	0.2167 (10)	0.20459 (17)	0.1186 (7)	0.1147 (17)
H1A	0.628 (7)	0.4740 (17)	0.220 (5)	0.032 (9)*
H1B	0.818 (8)	0.4609 (19)	0.334 (6)	0.053 (13)*
H1WA	0.813 (10)	0.565 (2)	0.376 (7)	0.075 (17)*
H1WB	0.621 (10)	0.595 (3)	0.379 (7)	0.071 (18)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0308 (4)	0.0154 (3)	0.0324 (4)	-0.0018 (2)	0.0046 (2)	-0.0005 (2)
O1W	0.0446 (15)	0.0204 (11)	0.0499 (15)	-0.0021 (10)	0.0169 (12)	0.0013 (10)
N1	0.0377 (15)	0.0218 (12)	0.0287 (14)	-0.0019 (11)	0.0008 (12)	-0.0001 (11)
O3	0.0377 (13)	0.0797 (19)	0.0313 (13)	-0.0009 (13)	0.0027 (10)	0.0111 (12)
O4	0.0581 (16)	0.0696 (19)	0.0397 (15)	0.0147 (14)	0.0168 (12)	0.0132 (13)

N3	0.0356 (15)	0.0397 (15)	0.0352 (15)	0.0028 (12)	-0.0034 (12)	0.0006 (12)
C1	0.0340 (16)	0.0215 (14)	0.0294 (15)	-0.0018 (12)	0.0060 (12)	-0.0035 (12)
O2	0.176 (4)	0.0286 (16)	0.088 (3)	0.001 (2)	0.034 (3)	-0.0019 (17)
O5	0.0543 (19)	0.124 (3)	0.079 (2)	0.039 (2)	-0.0156 (17)	0.020 (2)
C6	0.0439 (19)	0.0309 (17)	0.0389 (18)	-0.0031 (15)	0.0005 (15)	-0.0043 (14)
N2	0.121 (4)	0.038 (2)	0.061 (3)	-0.017 (2)	0.036 (3)	-0.0115 (18)
C2	0.0434 (19)	0.0308 (17)	0.046 (2)	0.0057 (15)	0.0022 (16)	-0.0030 (15)
C4	0.074 (3)	0.0274 (18)	0.047 (2)	-0.0150 (18)	0.019 (2)	-0.0110 (15)
C5	0.056 (2)	0.041 (2)	0.049 (2)	-0.0184 (18)	0.0041 (18)	-0.0133 (17)
C3	0.078 (3)	0.0278 (18)	0.055 (2)	0.0184 (18)	0.018 (2)	0.0068 (16)
O1	0.138 (4)	0.059 (2)	0.146 (4)	-0.045 (3)	-0.002 (4)	-0.036 (2)

Geometric parameters (Å, °)

Cu1—O1W	1.996 (2)	C1—C6	1.389 (5)
Cu1—O1W ⁱ	1.996 (2)	C1—C2	1.373 (5)
Cu1—N1	2.055 (3)	O2—N2	1.209 (6)
Cu1—N1 ⁱ	2.055 (3)	C6—H6	0.9300
Cu1—O3 ⁱ	2.367 (2)	C6—C5	1.368 (5)
Cu1—O3	2.367 (2)	N2—C4	1.485 (5)
O1W—H1WA	0.81 (6)	N2—O1	1.229 (6)
O1W—H1WB	0.76 (6)	C2—H2	0.9300
N1—C1	1.431 (4)	C2—C3	1.403 (5)
N1—H1A	0.82 (4)	C4—C5	1.363 (6)
N1—H1B	0.86 (4)	C4—C3	1.367 (6)
O3—N3	1.272 (4)	C5—H5	0.9300
O4—N3	1.219 (4)	C3—H3	0.9300
N3—O5	1.217 (4)		
O1W—Cu1—O1W ⁱ	180.0	O4—N3—O3	119.4 (3)
O1W ⁱ —Cu1—N1 ⁱ	87.62 (11)	O5—N3—O3	117.8 (3)
O1W ⁱ —Cu1—N1	92.38 (11)	O5—N3—O4	122.8 (3)
O1W—Cu1—N1 ⁱ	92.38 (11)	C6—C1—N1	118.3 (3)
O1W—Cu1—N1	87.62 (11)	C2—C1—N1	120.8 (3)
O1W—Cu1—O3 ⁱ	85.93 (12)	C2—C1—C6	120.9 (3)
O1W—Cu1—O3	94.07 (12)	C1—C6—H6	120.1
O1W ⁱ —Cu1—O3 ⁱ	94.07 (12)	C5—C6—C1	119.9 (3)
O1W ⁱ —Cu1—O3	85.93 (12)	C5—C6—H6	120.1
N1 ⁱ —Cu1—N1	180.0	O2—N2—C4	117.7 (5)
N1 ⁱ —Cu1—O3 ⁱ	95.99 (11)	O2—N2—O1	124.6 (4)
N1—Cu1—O3 ⁱ	84.01 (11)	O1—N2—C4	117.7 (5)
N1 ⁱ —Cu1—O3	84.01 (11)	C1—C2—H2	120.6
N1—Cu1—O3	95.99 (11)	C1—C2—C3	118.7 (4)
O3 ⁱ —Cu1—O3	180.0	C3—C2—H2	120.6
Cu1—O1W—H1WA	117 (4)	C5—C4—N2	118.1 (4)
Cu1—O1W—H1WB	116 (4)	C5—C4—C3	122.4 (3)
H1WA—O1W—H1WB	105 (5)	C3—C4—N2	119.5 (4)
Cu1—N1—H1A	101 (3)	C6—C5—H5	120.4

Cu1—N1—H1B	100 (3)	C4—C5—C6	119.2 (4)
C1—N1—Cu1	120.2 (2)	C4—C5—H5	120.4
C1—N1—H1A	111 (3)	C2—C3—H3	120.5
C1—N1—H1B	114 (3)	C4—C3—C2	118.9 (4)
H1A—N1—H1B	109 (4)	C4—C3—H3	120.5
N3—O3—Cu1	122.4 (2)		
Cu1—N1—C1—C6	81.0 (3)	O2—N2—C4—C3	-5.9 (6)
Cu1—N1—C1—C2	-97.5 (3)	C6—C1—C2—C3	0.7 (5)
Cu1—O3—N3—O4	17.1 (4)	N2—C4—C5—C6	179.5 (4)
Cu1—O3—N3—O5	-163.2 (3)	N2—C4—C3—C2	-178.6 (4)
N1—C1—C6—C5	-178.4 (3)	C2—C1—C6—C5	0.2 (5)
N1—C1—C2—C3	179.2 (3)	C5—C4—C3—C2	1.6 (6)
C1—C6—C5—C4	-0.2 (6)	C3—C4—C5—C6	-0.7 (6)
C1—C2—C3—C4	-1.6 (6)	O1—N2—C4—C5	-5.2 (6)
O2—N2—C4—C5	173.9 (4)	O1—N2—C4—C3	175.0 (4)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O4	0.82 (4)	2.30 (4)	3.021 (4)	147 (4)
O1 <i>W</i> —H1 <i>WA</i> \cdots O3 ⁱⁱ	0.81 (5)	2.07 (5)	2.828 (4)	156 (5)
O1 <i>W</i> —H1 <i>WA</i> \cdots O5 ⁱⁱ	0.81 (5)	2.28 (5)	2.979 (5)	145 (5)
N1—H1A \cdots O4 ⁱⁱⁱ	0.82 (4)	2.42 (4)	3.057 (4)	135 (3)
N1—H1B \cdots O3 ⁱⁱ	0.86 (4)	2.34 (4)	3.103 (4)	148 (4)
N1—H1B \cdots O3 ⁱ	0.86 (4)	2.60 (5)	2.968 (4)	107 (3)
O1 <i>W</i> —H1 <i>WB</i> \cdots O1 ^{iv}	0.76 (6)	2.64 (5)	3.085 (5)	120 (5)
O1 <i>W</i> —H1 <i>WB</i> \cdots O2 ^{iv}	0.77 (6)	2.26 (6)	3.022 (5)	171 (5)

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