metal-organic papers

Diaquabis(ethylenediamine)copper(II) bis(4-nitrobenzoate)

William T. A. Harrison,[a]* **Alexandra M. Z. Slawin,**[b] **Raj Pal Sharma,**[c]* **Bhavna Sharma**[c] **and Shekar Bhama**[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, [b]Department of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, and [c]Panjab University, Department of Chemistry, Chandigarh 160 014, India

Correspondence e-mail:
w.harrison@abdn.ac.uk,
rpsharma@yahoo.co.in

Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.077
Data-to-parameter ratio = 12.5

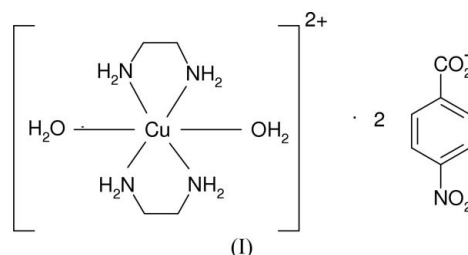For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Cu(C_2H_8N_2)_2(H_2O)_2](C_7H_4NO_4)_2$, the component complex cations and organic anions interact by way of N—H···O and O—H···O hydrogen bonds, leading to a layered structure. The Cu atom has site symmetry $\bar{1}$.

Comment

The title compound, (I), was prepared as part of our ongoing studies of second-sphere hydrogen-bonding interactions in compounds containing cationic metal complexes and organic counter-anions (Sharma, Bala *et al.*, 2006; Sharma, Sharma *et al.*, 2006).

(I)

The geometrical parameters for the component species in (I) fall within their expected ranges (Allen *et al.*, 1987). The well known $[Cu(C_2N_2H_8)_2(H_2O)_2]^{2+}$ complex cation in (I) is built up from a central copper(II) ion (site symmetry $\bar{1}$) chelated by two ethylenediamine molecules to form an approximate CuN_4 square. The Jahn–Teller distorted copper coordination is completed by two *trans* water molecules (Table 1). The Cu—N and Cu—O bond lengths in (I) are very similar to the equivalent values observed for the same complex cation in its bis(naphthalene-2-sulfonate) (Sharma *et al.*, 2005) and bis(4-fluorobenzoate) (Liu *et al.*, 2004) salts.

The 4-nitrobenzoate anion in (I) is almost planar, the dihedral angles between the mean plane of the C3–C8 benzene ring and the planes of its attached C9/O2/O3 carboxylate and N3/O4/O5 nitro groups being 2.14 (17) and 1.9 (2)°, respectively. The carboxylate C—O bond lengths are almost equal, suggesting charge delocalization.

As well as electrostatic forces, the component species in (I) interact by way of O—H···O and N—H···O hydrogen bonds (Table 2). Firstly, adjacent complex cations are linked into chains propagating along [100] by way of translation-related pairs of N1—H1···O1[i] bonds (see Table 2 for symmetry code). A bridging carboxylate atom O3 also helps to consolidate the chains (Fig. 2). Then, adjacent cations and anions form a distinctive bridged chain propagating along [010] (Fig. 3), where each carboxylate group in the chain accepts no fewer than four hydrogen bonds from its two adjoining cations.
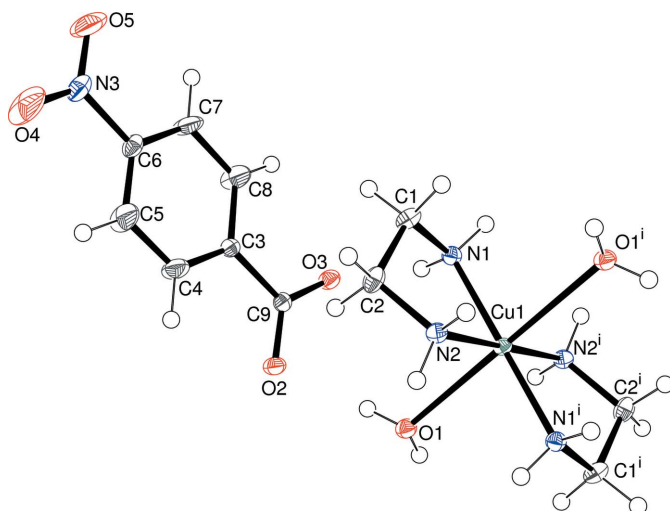
Figure 1
View of the molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]
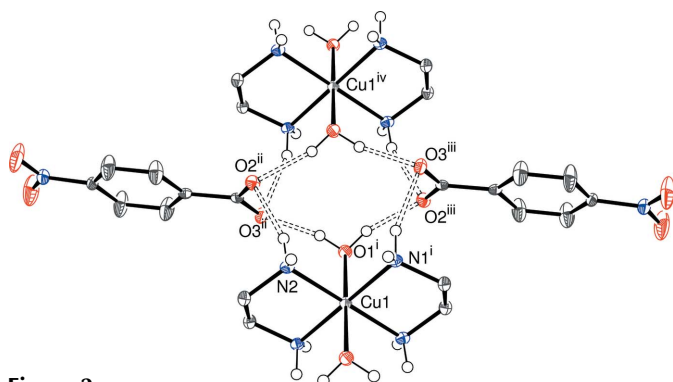

Figure 2
Detail of (I), showing part of a [100] chain arising from hydrogen-bonding interactions (dashed lines). C-bound H atoms have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $1 + x, y, z$; (iv) $1 + x, 1 + y, z$.]
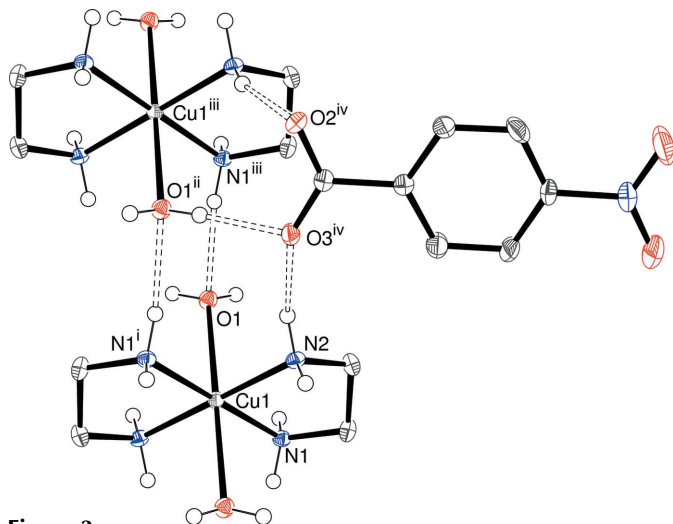

Figure 3
Detail of (I), showing part of a [010] chain arising from hydrogen-bonding interactions (dashed lines). C-bound H atoms have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $x, 1 + y, z$.]

Combining these hydrogen-bonding motifs results in (001) sheets of tightly bound cations and anions. It is notable that the nitro O atoms do not serve as acceptors for any of the hydrogen bonds.

Experimental

Compound (I) was prepared by taking a suspension of [Cu(H2O)6](C7H4NO4)2 [obtained by reacting basic copper(II) carbonate with *p*-nitrobenzoic acid in water] and adding a methanol solution of ethylenediamine dropwise until a slight excess of a 1:2 Cu–en stoichiometry was achieved, resulting in a deep-blue solution, which was allowed to evaporate at room temperature to obtain purple crystals of (I) after a few days. Crystals were filtered off and dried in air.

Crystal data

[Cu(C2H8N2)2(H2O)2](C7H4NO4)2	$V = 583.69 \ (15) \ Å^3$
$M_r = 552.00$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.570 \ \text{Mg m}^{-3}$
$a = 6.0019 \ (5) \ Å$	Mo $K\alpha$ radiation
$b = 7.1230 \ (4) \ Å$	$\mu = 1.00 \ \text{mm}^{-1}$
$c = 15.370 \ (2) \ Å$	$T = 93 \ (2) \ K$
$\alpha = 95.48 \ (2)°$	Cube, purple
$\beta = 98.43 \ (2)°$	$0.10 \times 0.10 \times 0.10 \ \text{mm}$
$\gamma = 114.26 \ (2)°$	

Data collection

Rigaku Mercury CCD diffractometer	3754 measured reflections
φ and ω scans	2005 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	1930 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.856, \ T_{\max} = 1.000$	$R_{\text{int}} = 0.015$
(expected range = 0.774–0.905)	$\theta_{\max} = 25.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.5044P]$
$wR(F^2) = 0.077$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\max} = 0.002$
2005 reflections	$\Delta\rho_{\max} = 0.43 \ \text{e} \ Å^{-3}$
160 parameters	$\Delta\rho_{\min} = -0.44 \ \text{e} \ Å^{-3}$
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Cu1—N1	2.0146 (18)	C9—O2	1.256 (3)
Cu1—N2	2.0272 (19)	C9—O3	1.261 (3)
Cu1—O1	2.5369 (17)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^i	0.92	2.11	3.018 (2)	170
N1—H2$\cdots$O3	0.92	2.20	3.081 (2)	161
N2—H3$\cdots$O3^{ii}	0.92	2.24	3.037 (3)	145
N2—H4$\cdots$O2^{iii}	0.92	2.07	2.960 (2)	162
O1—H5$\cdots$O3^{iv}	0.89	1.88	2.754 (2)	166
O1—H6$\cdots$O2	0.86	1.93	2.767 (2)	164

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

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The O-bound H atoms were located in a difference map and refined as riding in their as-found relative positions with $U_{iso}(H) = 1.2U_{eq}(O)$. The C- and N-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å, N—H = 0.92 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *CrystalClear* (Rigaku, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

Diaquabis(ethylenediamine)copper(II) bis(4-nitrobenzoate)

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Crystal data

$[Cu(C_2H_8N_2)_2(H_2O)_2](C_7H_4NO_4)_2$	$Z = 1$
$M_r = 552.00$	$F(000) = 287$
Triclinic, $P\bar{1}$	$D_x = 1.570$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.0019$ (5) Å	Cell parameters from 2340 reflections
$b = 7.1230$ (4) Å	$\theta = 2.7$–$28.2°$
$c = 15.370$ (2) Å	$\mu = 1.00$ mm^{-1}
$\alpha = 95.48$ (2)°	$T = 93$ K
$\beta = 98.43$ (2)°	Cube, purple
$\gamma = 114.26$ (2)°	$0.10 \times 0.10 \times 0.10$ mm
$V = 583.69$ (15) Å^3	

Data collection

Rigaku Mercury CCD diffractometer	3754 measured reflections
Radiation source: rotating anode	2005 independent reflections
Confocal monochromator	1930 reflections with $I > 2\sigma(I)$
Detector resolution: 0.83 pixels mm^{-1}	$R_{int} = 0.015$
φ and ω scans	$\theta_{max} = 25.3°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -5 \rightarrow 7$
	$k = -6 \rightarrow 8$
$T_{min} = 0.856$, $T_{max} = 1.000$	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.077$	
$S = 1.08$	H-atom parameters constrained
2005 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.5044P]$ where $P = (F_o^2 + 2F_c^2)/3$
160 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.002$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.43$ e Å^{-3}
	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.5000	0.5000	0.5000	0.01301 (14)
C1	0.3527 (4)	0.4877 (4)	0.66944 (15)	0.0177 (5)
H1A	0.2872	0.4000	0.7143	0.021*
H1B	0.2922	0.5978	0.6710	0.021*
C2	0.6352 (4)	0.5864 (4)	0.69053 (15)	0.0177 (5)
H2A	0.6998	0.6899	0.7465	0.021*
H2B	0.6960	0.4780	0.6983	0.021*
N1	0.2647 (3)	0.3572 (3)	0.57892 (12)	0.0131 (4)
H1	0.1061	0.3396	0.5551	0.016*
H2	0.2599	0.2274	0.5826	0.016*
N2	0.7230 (3)	0.6905 (3)	0.61493 (12)	0.0138 (4)
H3	0.8861	0.7141	0.6160	0.017*
H4	0.7145	0.8170	0.6191	0.017*
O1	0.7238 (3)	0.2674 (2)	0.51837 (10)	0.0158 (4)
H5	0.7064	0.1756	0.4710	0.019*
H6	0.6952	0.1896	0.5589	0.019*
C3	0.4867 (4)	0.1037 (3)	0.78913 (14)	0.0139 (5)
C4	0.7093 (5)	0.2037 (5)	0.85044 (17)	0.0297 (6)
H4A	0.8620	0.2341	0.8313	0.036*
C5	0.7131 (5)	0.2603 (5)	0.93950 (17)	0.0354 (7)
H5A	0.8666	0.3270	0.9818	0.042*
C6	0.4916 (4)	0.2183 (3)	0.96539 (15)	0.0167 (5)
C7	0.2672 (5)	0.1185 (5)	0.90654 (17)	0.0350 (7)
H7	0.1152	0.0891	0.9262	0.042*
C8	0.2663 (5)	0.0614 (5)	0.81761 (17)	0.0330 (7)
H8	0.1120	−0.0078	0.7759	0.040*
C9	0.4873 (4)	0.0454 (3)	0.69155 (14)	0.0136 (5)
N3	0.4942 (4)	0.2855 (3)	1.05959 (13)	0.0222 (5)
O2	0.6956 (3)	0.0885 (2)	0.67087 (10)	0.0171 (4)
O3	0.2795 (3)	−0.0400 (2)	0.63757 (10)	0.0183 (4)
O4	0.6929 (4)	0.3750 (4)	1.11118 (13)	0.0516 (6)
O5	0.2963 (4)	0.2486 (4)	1.08147 (13)	0.0499 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0109 (2)	0.0139 (2)	0.0121 (2)	0.00344 (16)	0.00238 (15)	0.00153 (15)
C1	0.0215 (13)	0.0168 (13)	0.0140 (11)	0.0066 (10)	0.0070 (10)	0.0020 (9)
C2	0.0204 (13)	0.0176 (13)	0.0124 (11)	0.0065 (10)	0.0012 (10)	0.0017 (9)
N1	0.0124 (9)	0.0120 (10)	0.0152 (9)	0.0059 (8)	0.0019 (8)	0.0018 (7)
N2	0.0111 (9)	0.0127 (10)	0.0172 (10)	0.0048 (8)	0.0037 (8)	0.0017 (8)
O1	0.0175 (8)	0.0155 (8)	0.0158 (8)	0.0080 (7)	0.0046 (7)	0.0032 (6)
C3	0.0172 (12)	0.0093 (12)	0.0164 (11)	0.0067 (9)	0.0034 (9)	0.0025 (9)
C4	0.0155 (13)	0.0513 (18)	0.0181 (13)	0.0107 (12)	0.0046 (10)	0.0028 (12)
C5	0.0165 (14)	0.0567 (19)	0.0168 (13)	0.0039 (13)	−0.0026 (11)	−0.0018 (12)
C6	0.0261 (13)	0.0135 (12)	0.0118 (11)	0.0096 (10)	0.0050 (10)	0.0015 (9)
C7	0.0181 (14)	0.063 (2)	0.0184 (13)	0.0124 (13)	0.0080 (11)	−0.0036 (13)
C8	0.0153 (13)	0.0508 (18)	0.0197 (13)	0.0038 (12)	0.0034 (11)	−0.0050 (12)
C9	0.0191 (12)	0.0086 (11)	0.0152 (11)	0.0073 (9)	0.0047 (10)	0.0037 (9)
N3	0.0327 (13)	0.0195 (11)	0.0138 (10)	0.0106 (10)	0.0052 (10)	0.0020 (8)
O2	0.0167 (8)	0.0188 (9)	0.0183 (8)	0.0086 (7)	0.0075 (7)	0.0038 (7)
O3	0.0162 (9)	0.0215 (9)	0.0135 (8)	0.0054 (7)	0.0027 (7)	−0.0005 (6)
O4	0.0385 (13)	0.0721 (16)	0.0171 (10)	0.0033 (11)	0.0003 (10)	−0.0118 (10)
O5	0.0417 (13)	0.0851 (18)	0.0219 (11)	0.0273 (12)	0.0131 (10)	−0.0052 (11)

Geometric parameters (Å, º)

Cu1—N1^i	2.0146 (18)	O1—H6	0.8625
Cu1—N1	2.0146 (18)	C3—C8	1.378 (3)
Cu1—N2	2.0272 (19)	C3—C4	1.379 (3)
Cu1—N2^i	2.0272 (19)	C3—C9	1.519 (3)
Cu1—O1	2.5369 (17)	C4—C5	1.384 (4)
Cu1—O1^i	2.5369 (17)	C4—H4A	0.950
C1—N1	1.488 (3)	C5—C6	1.366 (4)
C1—C2	1.513 (3)	C5—H5A	0.950
C1—H1A	0.990	C6—C7	1.368 (4)
C1—H1B	0.990	C6—N3	1.477 (3)
C2—N2	1.483 (3)	C7—C8	1.387 (4)
C2—H2A	0.990	C7—H7	0.950
C2—H2B	0.990	C8—H8	0.950
N1—H1	0.920	C9—O2	1.256 (3)
N1—H2	0.920	C9—O3	1.261 (3)
N2—H3	0.920	N3—O4	1.208 (3)
N2—H4	0.920	N3—O5	1.212 (3)
O1—H5	0.8941		
N1^i—Cu1—N1	180.0	H1—N1—H2	108.3
N1^i—Cu1—N2	95.08 (7)	C2—N2—Cu1	107.93 (14)
N1—Cu1—N2	84.92 (7)	C2—N2—H3	110.1
N1^i—Cu1—N2^i	84.92 (7)	Cu1—N2—H3	110.1
N1—Cu1—N2^i	95.08 (7)	C2—N2—H4	110.1

N2—Cu1—N2ⁱ	180.0	Cu1—N2—H4	110.1
O1—Cu1—N1	92.58 (7)	H3—N2—H4	108.4
O1—Cu1—N2	89.44 (7)	H5—O1—H6	101.3
O1—Cu1—N1ⁱ	87.42 (7)	C8—C3—C4	119.0 (2)
O1—Cu1—N2ⁱ	90.56 (7)	C8—C3—C9	121.0 (2)
O1ⁱ—Cu1—N1ⁱ	92.58 (7)	C4—C3—C9	119.9 (2)
O1ⁱ—Cu1—N2ⁱ	89.44 (7)	C3—C4—C5	120.9 (2)
O1ⁱ—Cu1—N1	87.42 (7)	C3—C4—H4A	119.6
O1ⁱ—Cu1—N2	90.56 (7)	C5—C4—H4A	119.6
O1—Cu1—O1ⁱ	180.0	C6—C5—C4	118.6 (2)
N1—C1—C2	108.30 (18)	C6—C5—H5A	120.7
N1—C1—H1A	110.0	C4—C5—H5A	120.7
C2—C1—H1A	110.0	C5—C6—C7	122.1 (2)
N1—C1—H1B	110.0	C5—C6—N3	119.1 (2)
C2—C1—H1B	110.0	C7—C6—N3	118.8 (2)
H1A—C1—H1B	108.4	C6—C7—C8	118.6 (2)
N2—C2—C1	107.83 (18)	C6—C7—H7	120.7
N2—C2—H2A	110.1	C8—C7—H7	120.7
C1—C2—H2A	110.1	C3—C8—C7	120.8 (2)
N2—C2—H2B	110.1	C3—C8—H8	119.6
C1—C2—H2B	110.1	C7—C8—H8	119.6
H2A—C2—H2B	108.5	O2—C9—O3	125.2 (2)
C1—N1—Cu1	109.03 (13)	O2—C9—C3	117.2 (2)
C1—N1—H1	109.9	O3—C9—C3	117.57 (19)
Cu1—N1—H1	109.9	O4—N3—O5	123.0 (2)
C1—N1—H2	109.9	O4—N3—C6	118.6 (2)
Cu1—N1—H2	109.9	O5—N3—C6	118.4 (2)
N1—C1—C2—N2	51.7 (2)	N3—C6—C7—C8	178.1 (2)
C2—C1—N1—Cu1	−36.6 (2)	C4—C3—C8—C7	0.2 (4)
N2—Cu1—N1—C1	11.08 (14)	C9—C3—C8—C7	−178.8 (3)
N2ⁱ—Cu1—N1—C1	−168.92 (14)	C6—C7—C8—C3	0.1 (5)
C1—C2—N2—Cu1	−41.2 (2)	C8—C3—C9—O2	−179.8 (2)
N1ⁱ—Cu1—N2—C2	−163.03 (14)	C4—C3—C9—O2	1.3 (3)
N1—Cu1—N2—C2	16.97 (14)	C8—C3—C9—O3	1.1 (3)
C8—C3—C4—C5	0.3 (4)	C4—C3—C9—O3	−177.8 (2)
C9—C3—C4—C5	179.3 (2)	C5—C6—N3—O4	−0.3 (4)
C3—C4—C5—C6	−1.1 (4)	C7—C6—N3—O4	−179.4 (3)
C4—C5—C6—C7	1.4 (4)	C5—C6—N3—O5	179.4 (3)
C4—C5—C6—N3	−177.6 (2)	C7—C6—N3—O5	0.4 (4)
C5—C6—C7—C8	−0.9 (4)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1ⁱⁱ	0.92	2.11	3.018 (2)	170

N1—H2···O3	0.92	2.20	3.081 (2)	161
N2—H3···O3ⁱⁱⁱ	0.92	2.24	3.037 (3)	145
N2—H4···O2ⁱᵛ	0.92	2.07	2.960 (2)	162
O1—H5···O3ᵛ	0.89	1.88	2.754 (2)	166
O1—H6···O2	0.86	1.93	2.767 (2)	164

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