

Otávio Versiane,^a Judith Felcman,^a Jussara Lopes de Miranda,^b R. Alan Howie^c and Janet M. S. Skakle^{c*}

^aDepartamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente 225, Gávea, 22453-999 Rio de Janeiro, RJ, Brazil,

^bDepartamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil, and ^cDepartment of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: j.skakle@abdn.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 Disorder in solvent or counterion
 R factor = 0.019
 wR factor = 0.052
 Data-to-parameter ratio = 15.1

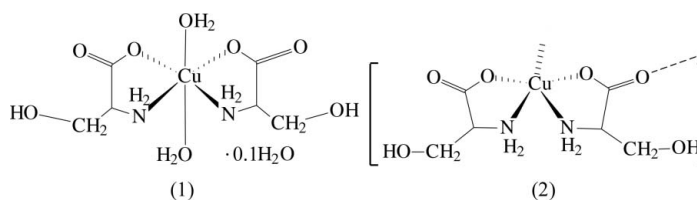
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Diaquabis(L-serinato)copper(II) 0.1-hydrate at 120 K

The title compound, $[\text{Cu}(\text{C}_3\text{H}_6\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 0.1\text{H}_2\text{O}$, is isostructural with the nickel analogue. The octahedral Cu^{II} ion lies on a twofold axis, with *cis* chelating *O,N*-serine groups and *trans* aqua ligands. Small amounts of a solvent water molecule form hydrogen bonds to link the molecules along the [010] direction, while a number of strong hydrogen bonds combine to form sheets in the (110) plane.

Comment

As part of our continuing study of Cu complexes with amino acids (Felcman & de Miranda, 1997; de Miranda & Felcman, 2001; de Miranda *et al.*, 2002; Felcman *et al.*, 2003), we have isolated and characterized the diaquabis(L-serinato)-copper(II) complex, (1), from an aqueous reaction mixture containing (*L*)-serine (ser), guanidinoacetic acid (gaa) and Cu^{II} (1:1:1). Crystals of (1) were obtained after several months. No crystalline complex containing gaa, either alone or in a mixed complex with ser, appeared in a similar time. van der Helm & Franks (1969) reported the structure of the unhydrated complex, [bis(L-serinato)copper(II)], (2), obtained from Cu^{II} and (*L*)-serine in methanol containing a little water.



Complex (1), isostructural with the analogous nickel complex, diaquabis(L-serinato)nickel(II) hydrate, (3), (van der Helm & Hossain, 1969), has an octahedrally coordinated Cu^{II} ion with *cis* chelating *O,N*-ser groups and *trans* aqua ligands (Fig. 1). A similar *cis* arrangement of ser units arises in square-pyramidal (2), in which a carboxylate O atom, from an adjacent molecule, occupies the apical position. A distant O atom is sited 3.632 (6) Å from Cu *trans* to the apical ligand in (2), but this can at most be considered only a very weak interaction. Comparison of the serine–Cu bond lengths in (2) [Cu–O 1.952 (5) and 1.970 (5) Å; Cu–N 1.975 (6) and 1.988 (6) Å] and in (1) (Table 1) indicates that the weaker interactions occur in the higher coordinate complex, (1). The serine chelate rings in (1) have envelope conformations with flaps at the N atoms. The Cu^{II} ion and the four serine binding atoms are essentially co-planar.

Small amounts of additional water molecules are present in both (1) and (3). The space group and structure of (1) are notably different from those of the unhydrated compound, (2), and although only a very small amount of water was found

Received 26 October 2005

Accepted 27 October 2005

Online 5 November 2005

to be present in (1), both the hydrogen-bonding scheme (see below) and the availability of space (PLATON; Spek, 2003) confirm its presence.

The non-isolation of any gaa-containing complex from the reaction mixture probably reflects more their solubility in the reaction media than their non-formation. A number of Cu-gaa complexes have been isolated, including tetrakis(μ -guanidinoacetic acid- $\kappa^2O:O'$)bis[nitrato- κO]copper, [Cu₂(NO₃)₂(gaa)₄], (4) (de Miranda *et al.*, 2002), {aqua[μ -(*N'*-carboxylatomethylguanidino)oxidoacetato](μ -guanidinoacetic acid)dicopper(II)} nitrate dihydrate, [Cu₂(oag)(gaa)(H₂O)]NO₃·2H₂O, (5) (Felcman *et al.*, 2003), and [CuCl₂(gaa)₂] (Silva *et al.*, 2001). Compounds (4) and (5) were obtained from reaction mixtures containing gaa and Cu^{II}, both in the presence and absence of another amino acid, namely aspartine. Furthermore, mixed Cu-L-serine complexes, *e.g.* with glycine, have been reported (D'yakon *et al.*, 1991).

The solvent water molecule forms hydrogen bonds (Table 2) with the O atom of the aqua ligand in the main molecule (Fig. 2), leading to chains along [010]. Together with the other strong hydrogen bonds (Table 2), these form sheets in the (110) plane (Fig. 2).

Experimental

To a hot solution (333 K) of guanidinoacetic acid (0.3513 g, 3 mmol) and serine (0.3153, 3 mmol) in deionized water (100 ml) was slowly added a solution of copper(II) nitrate (0.7248 g, 3 mmol) in deionized water (5 ml). The reaction mixture was stirred at 333 K for 8 h, cooled slowly to 277 K, and the pH adjusted to 6.0 with KOH (3 M). The white precipitate which formed was filtered off and the filtrate was stored in a covered vessel. Thin blue plate-like crystals began to be formed after the fifth month and were collected after six months, washed with absolute ethanol and dried at 323 K.

Crystal data

[Cu(C ₃ H ₆ NO ₃) ₂ (H ₂ O) ₂].0.1H ₂ O	$D_x = 1.837 \text{ Mg m}^{-3}$
$M_r = 309.55$	Mo $K\alpha$ radiation
Monoclinic, $C2$	Cell parameters from 673 reflections
$a = 7.5866 (2) \text{ \AA}$	$\theta = 2.9\text{--}27.5^\circ$
$b = 8.5684 (2) \text{ \AA}$	$\mu = 1.99 \text{ mm}^{-1}$
$c = 8.8257 (2) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 102.7701 (15)^\circ$	Plate, pale blue
$V = 559.52 (2) \text{ \AA}^3$	$0.40 \times 0.30 \times 0.08 \text{ mm}$
$Z = 2$	

Data collection

Bruker Nonius KappaCCD area-detector diffractometer	1220 independent reflections
φ and ω scans	1214 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.026$
$T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.853$	$\theta_{\text{max}} = 27.5^\circ$
3347 measured reflections	$h = -7 \rightarrow 9$
	$k = -10 \rightarrow 11$
	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0104P)^2 + 0.5389P]$
$R[F^2 > 2\sigma(F^2)] = 0.019$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.053$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
1220 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
81 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	with 536 Friedel pairs
	Flack parameter: 0.071 (12)

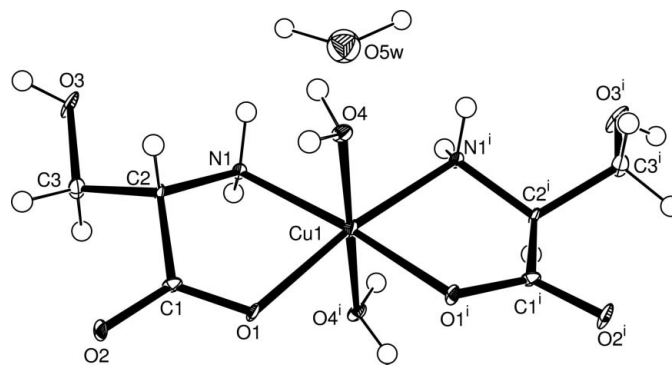


Figure 1
The molecular structure of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as open circles. [Symmetry code: (i) 1 - x, y, -z.]

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—O1	2.032 (2)	Cu1—O4	2.1044 (11)
Cu1—N1	2.079 (2)		
O1—Cu1—O1 ⁱ	91.50 (11)	O1—Cu1—O4 ⁱ	87.95 (8)
O1—Cu1—N1 ⁱ	172.11 (9)	N1—Cu1—O4 ⁱ	89.99 (8)
O1—Cu1—N1	81.16 (7)	N1—Cu1—O4	89.49 (8)
N1—Cu1—N1 ⁱ	106.31 (13)	O4—Cu1—O4 ⁱ	179.14 (14)
O1—Cu1—O4	92.65 (8)		

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

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O2 ⁱⁱ	0.92	2.39	3.154 (3)	141
N1—H1B \cdots O1 ⁱⁱⁱ	0.92	2.25	3.071 (2)	149
O3—H3 \cdots O2 ^{iv}	0.84	1.84	2.671 (2)	172
O4—H4A \cdots O3 ^v	0.82	1.90	2.701 (3)	168
O4—H4B \cdots O2 ⁱⁱ	0.81	1.94	2.747 (3)	177
O5W—H5 \cdots O4 ^{vi}	0.82	2.18	2.807 (4)	134

Symmetry codes: (ii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (v) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (vi) $-x + \frac{3}{2}, y + \frac{1}{2}, -z$.

Systematic absences permitted $C2$, Cm and $C2/m$ as possible space groups; $C2$ was selected and confirmed by the subsequent structure analysis. In this space group, atoms Cu1 and O5W of the low-occupancy solvent water molecule (see below) lie on crystallographic twofold axes. Therefore, the asymmetric unit comprises, in addition to these two atoms, one of each of a complete serinate and aqua ligand and a single H atom of the solvent water molecule. The small amount of solvent water was clearly identified from the difference map. During the structure solution, and prior to the location of the water molecule, the difference map revealed two electron-density peaks close to one another, which suggested disorder of the water over two sites. However, the two positions could not be refined simultaneously and indeed, once one O atom was refined, the peak in the difference map corresponding to the 'second site' disappeared. Approximate positions for the H atoms of the aqua ligand and of the low-occupancy solvent water molecule were then obtained from difference maps and modified to provide acceptable O—H distances (0.81–0.82 \AA) and H—O—H angles (103°). Owing to correlation with the isotropic displacement parameter, the occupancy of the solvent water

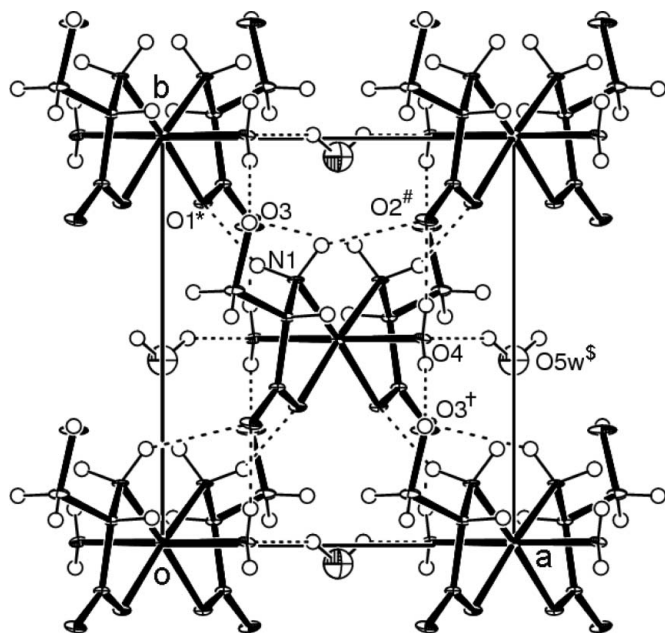


Figure 2

Part of the crystal structure of (1), showing the formation of sheets in the (110) plane built from N—H···O and O—H···O hydrogen bonds (dashed lines). Atoms labelled with a hash (#), asterisk (*) or plus sign (+) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} + y, z)$, $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$ and $(\frac{1}{2} + x, -\frac{1}{2} + y, z)$, respectively. The solvent water molecule is linked to the main molecule by the symmetry operation $(\frac{3}{2} - x, \frac{1}{2} + y, -z)$. The O3—H3···O2^{iv} hydrogen bond is not visible in this orientation but forms behind atom O3.

molecule could only be established by trial and error. The value of 0.10 finally chosen was such as to provide a reasonable value for the freely refined isotropic displacement parameter of the O atom (O5W). All other H atoms were placed in calculated positions, with X—H distances of 0.99 (CH₂), 1.00 (aliphatic CH), 0.92 (NH₂) or 0.84 Å (OH). The torsion angle of the OH group was also refined. All H atoms were refined, finally, with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL-X* (McArdle, 1994, 2005) and *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *OSCAIL-X* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

The authors thank CNPq and FAPERJ, Brazil, for support, and the EPSRC X-ray Crystallographic Service, University of Southampton, UK, for the data collection. In addition, we acknowledge the help and advice of J. L. Wardell.

References

- D'yakon, I. A., Donu, S. V., Chapurina, L. F. & Avilov, A. S. (1991). *Kristallografiya*, **31**, 219–221.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.
- Felcman, J., Howie, R. A., Miranda, J. L. de, Skakle, J. M. S. & Wardell, J. L. (2003). *Acta Cryst.* **C59**, m103–m106.
- Felcman, J. & Miranda, J. L. de (1997). *J. Braz. Chem. Soc.* **8**, 575–580.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Helm, D. van der & Franks, W. A. (1969). *Acta Cryst.* **B25**, 451–457.
- Helm, D. van der & Hossain, M. B. (1969). *Acta Cryst.* **B25**, 457–463.
- McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.
- McArdle, P. (2005). *OSCAIL-X for Windows*. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- Miranda, J. L. de & Felcman, J. (2001). *Synth. React. Inorg. Met. Chem.* **31**, 873–894.
- Miranda, J. L. de, Felcman, J., Wardell, J. L. & Skakle, J. M. S. (2002). *Acta Cryst.* **C58**, m471–m474.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97* and *CIFTAB*. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Silva, M. R., Paixão, J. A., Beja, A. M. & Veiga, L. A. (2001). *Acta Cryst.* **C57**, 7–8.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2005). E61, m2517–m2519 [https://doi.org/10.1107/S1600536805035221]

Diaquabis(L-serinato)copper(II) 0.1-hydrate at 120 K

Otávio Versiane, Judith Felcman, Jussara Lopes de Miranda, R. Alan Howie and Janet M. S. Skakle

diaquabis(L-serinato)copper(II) decihydrate

Crystal data

[Cu(C₃H₆NO₃)₂(H₂O)₂].0.1H₂O

$M_r = 309.55$

Monoclinic, C2

Hall symbol: C 2y

$a = 7.5866$ (2) Å

$b = 8.5684$ (2) Å

$c = 8.8257$ (2) Å

$\beta = 102.7701$ (15)°

$V = 559.52$ (2) Å³

$Z = 2$

$F(000) = 320$

$D_x = 1.837$ Mg m⁻³

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

Cell parameters from 673 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 1.99$ mm⁻¹

$T = 120$ K

Plate, pale blue

$0.40 \times 0.30 \times 0.08$ mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer

Radiation source: Bruker Nonius FR591 rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.666$, $T_{\max} = 0.853$

3347 measured reflections

1220 independent reflections

1214 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 4.0$ °

$h = -7 \rightarrow 9$

$k = -10 \rightarrow 11$

$l = -11 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.053$

$S = 1.10$

1220 reflections

81 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: geom and difmap

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0104P)^2 + 0.5389P]$

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

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

$\Delta\rho_{\max} = 0.29$ e Å⁻³

$\Delta\rho_{\min} = -0.44$ e Å⁻³

Absolute structure: Flack (1983), with 536 Friedel pairs

Absolute structure parameter: 0.071 (12)

Special details

Experimental. Although determined using *DIRAX*, the cell is refined during data reduction *DIRAX* refs: Duisenberg AJM, J. Appl. Cryst. 1992 25 92–96 and Duisenberg AJM, Hooft RWW, Schreurs AMM, Droon J.: J. Appl. Cryst. 2000 33 893–898

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.5000	0.5000	0.0000	0.00801 (11)	
O1	0.3839 (3)	0.3345 (2)	0.1111 (2)	0.0070 (4)	
O2	0.2506 (2)	0.2929 (2)	0.30727 (18)	0.0105 (3)	
O3	0.2453 (3)	0.7763 (2)	0.38982 (18)	0.0150 (4)	
H3	0.2571	0.7839	0.4864	0.022*	
N1	0.3790 (3)	0.6455 (3)	0.1359 (3)	0.0061 (5)	
H1A	0.4516	0.7304	0.1686	0.007*	
H1B	0.2695	0.6807	0.0794	0.007*	
C1	0.3257 (3)	0.3816 (3)	0.2255 (3)	0.0066 (4)	
C2	0.3529 (3)	0.5539 (3)	0.2706 (3)	0.0057 (4)	
H2	0.4682	0.5609	0.3512	0.007*	
C3	0.2045 (3)	0.6195 (3)	0.3435 (3)	0.0107 (4)	
H3A	0.0871	0.6151	0.2674	0.013*	
H3B	0.1945	0.5558	0.4349	0.013*	
O4	0.73885 (15)	0.5018 (3)	0.17483 (13)	0.0081 (3)	
H4A	0.7519	0.4420	0.2483	0.012*	
H4B	0.7402	0.5867	0.2162	0.012*	
O5W	0.5000	0.947 (3)	0.0000	0.014 (5)*	0.10
H5	0.5356	1.0067	−0.0597	0.020*	0.10

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01260 (16)	0.00605 (17)	0.00643 (17)	0.000	0.00435 (11)	0.000
O1	0.0129 (9)	0.0053 (9)	0.0040 (8)	−0.0007 (7)	0.0044 (7)	−0.0013 (7)
O2	0.0204 (9)	0.0067 (8)	0.0070 (8)	−0.0030 (7)	0.0087 (7)	0.0006 (7)
O3	0.0377 (11)	0.0045 (8)	0.0054 (8)	−0.0004 (7)	0.0105 (7)	−0.0013 (7)
N1	0.0111 (11)	0.0018 (10)	0.0065 (11)	0.0000 (8)	0.0044 (8)	0.0003 (8)
C1	0.0097 (10)	0.0029 (11)	0.0065 (11)	0.0003 (9)	0.0004 (9)	−0.0002 (9)
C2	0.0107 (10)	0.0044 (11)	0.0032 (10)	−0.0005 (8)	0.0042 (8)	0.0005 (8)
C3	0.0184 (12)	0.0048 (10)	0.0117 (11)	−0.0002 (9)	0.0095 (9)	−0.0008 (9)
O4	0.0133 (6)	0.0046 (6)	0.0063 (6)	−0.0016 (11)	0.0020 (5)	0.0009 (11)

Geometric parameters (Å, °)

Cu1—O1 ⁱ	2.032 (2)	N1—H1A	0.9200
Cu1—O1	2.032 (2)	N1—H1B	0.9200
Cu1—N1	2.079 (2)	C1—C2	1.531 (4)
Cu1—N1 ⁱ	2.079 (2)	C2—C3	1.522 (3)
Cu1—O4 ⁱ	2.1044 (11)	C2—H2	1.0000
Cu1—O4	2.1044 (11)	C3—H3A	0.9900
O1—C1	1.255 (3)	C3—H3B	0.9900
O2—C1	1.267 (3)	O4—H4A	0.8154
O3—C3	1.419 (3)	O4—H4B	0.8126
O3—H3	0.8400	O5W—H5 ⁱ	0.8209
N1—C2	1.474 (3)	O5W—H5	0.8209
O1—Cu1—O1 ⁱ	91.50 (11)	Cu1—N1—H1B	110.2
O1 ⁱ —Cu1—N1	172.11 (9)	H1A—N1—H1B	108.5
O1—Cu1—N1 ⁱ	172.11 (9)	O1—C1—O2	123.2 (2)
O1—Cu1—N1	81.16 (7)	O1—C1—C2	117.9 (2)
O1 ⁱ —Cu1—N1 ⁱ	81.16 (7)	O2—C1—C2	118.8 (2)
N1—Cu1—N1 ⁱ	106.31 (13)	N1—C2—C3	112.8 (2)
O1—Cu1—O4	92.65 (8)	N1—C2—C1	109.8 (2)
O1 ⁱ —Cu1—O4 ⁱ	92.65 (8)	C3—C2—C1	113.3 (2)
O1 ⁱ —Cu1—O4	87.95 (8)	N1—C2—H2	106.8
O1—Cu1—O4 ⁱ	87.95 (8)	C3—C2—H2	106.8
N1 ⁱ —Cu1—O4	89.99 (8)	C1—C2—H2	106.8
N1—Cu1—O4 ⁱ	89.99 (8)	O3—C3—C2	109.65 (19)
N1—Cu1—O4	89.49 (8)	O3—C3—H3A	109.7
N1 ⁱ —Cu1—O4 ⁱ	89.49 (8)	C2—C3—H3A	109.7
O4—Cu1—O4 ⁱ	179.14 (14)	O3—C3—H3B	109.7
C1—O1—Cu1	115.53 (18)	C2—C3—H3B	109.7
C3—O3—H3	109.5	H3A—C3—H3B	108.2
C2—N1—Cu1	107.53 (16)	Cu1—O4—H4A	120.8
C2—N1—H1A	110.2	Cu1—O4—H4B	105.1
Cu1—N1—H1A	110.2	H4A—O4—H4B	102.5
C2—N1—H1B	110.2	H5 ⁱ —O5W—H5	103.1
O1 ⁱ —Cu1—O1—C1	164.3 (2)	Cu1—O1—C1—C2	-1.7 (3)
N1—Cu1—O1—C1	-12.74 (15)	Cu1—N1—C2—C3	-157.24 (16)
O4 ⁱ —Cu1—O1—C1	-103.05 (19)	Cu1—N1—C2—C1	-29.8 (2)
O4—Cu1—O1—C1	76.33 (19)	O1—C1—C2—N1	22.2 (3)
O1—Cu1—N1—C2	23.48 (14)	O2—C1—C2—N1	-159.7 (2)
N1 ⁱ —Cu1—N1—C2	-159.1 (2)	O1—C1—C2—C3	149.4 (2)
O4 ⁱ —Cu1—N1—C2	111.40 (17)	O2—C1—C2—C3	-32.6 (3)
O4—Cu1—N1—C2	-69.28 (17)	N1—C2—C3—O3	-57.8 (3)
Cu1—O1—C1—O2	-179.65 (16)	C1—C2—C3—O3	176.65 (18)

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

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>
N1—H1 <i>A</i> ...O2 ⁱⁱ	0.92	2.39	3.154 (3)	141
N1—H1 <i>B</i> ...O1 ⁱⁱⁱ	0.92	2.25	3.071 (2)	149
O3—H3...O2 ^{iv}	0.84	1.84	2.671 (2)	172
O4—H4 <i>A</i> ...O3 ^v	0.82	1.90	2.701 (3)	168
O4—H4 <i>B</i> ...O2 ⁱⁱ	0.81	1.94	2.747 (3)	177
O5 <i>W</i> —H5...O4 ^{vi}	0.82	2.18	2.807 (4)	134

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