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Poly[(μ_3-3,5-dinitrobenzoato-$\kappa^3O^1:O^{1'}:O^3$)(μ_2-hydroxido-$\kappa^2O:O$)-copper(II)]

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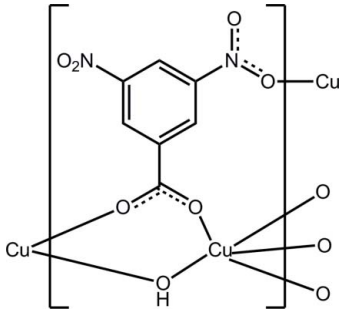
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.027; wR factor = 0.077; data-to-parameter ratio = 8.5.

The title complex, $[Cu\{\mu_3\text{-}O_2CC_6H_3(NO_2)_2\text{-}3,5\}(\mu\text{-}OH)]_n$, features zigzag chains in which successive pairs of Cu^{II} atoms are connected by OH bridges and bidentate carboxylate ligands, leading to six-membered Cu(O)(OCO)Cu rings. The zigzag chains are connected into a three-dimensional architecture by Cu—O(nitro) bonds. The coordination geometry of the Cu^{II} atom is square-pyramidal, with the axial position occupied by the nitro O atom, which forms the longer Cu—O bond. Bifurcated hydroxy–nitro O—H···O hydrogen bonds contribute to the stability of the crystal structure.

Related literature

For related Cu^{II} structures featuring Cu(μ_2-carboxylate)(μ_2-hydroxyl)Cu rings, see: You *et al.* (2005); Chen *et al.* (2006); Xiao *et al.* (2006). For additional structural analysis, see: Addison *et al.* (1984).



Experimental

Crystal data

$[Cu(C_7H_3N_2O_6)(OH)]$
M_r = 291.66
Orthorhombic, $Pna2_1$
a = 7.4665 (2) Å
b = 17.7858 (5) Å
c = 6.6821 (2) Å
V = 887.37 (4) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 3.87 mm^{-1}
T = 100 K
0.25 × 0.20 × 0.15 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.873, T_{max} = 1.000
3156 measured reflections
1324 independent reflections
1318 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.077
S = 1.05
1324 reflections
155 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}
Absolute structure: Flack (1983), 360 Friedel pairs
Absolute structure parameter: 0.06 (5)

Table 1
Selected bond lengths (Å).

Cu—O1	1.9689 (18)	Cu—O5^{ii}	2.5871 (18)
Cu—O7	1.899 (2)	Cu—O7^{i}	1.900 (2)
Cu—O2^{i}	1.9675 (18)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H1···O3^{iii}	0.84	2.52	3.190 (3)	137
O7—H1···O4^{iii}	0.84	2.57	3.271 (2)	142

Symmetry code: (iii) $-x-\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HG5386).

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supplementary materials

Acta Cryst. (2014). E**70**, m112–m113 [doi:10.1107/S1600536814004280]

Poly[(μ_3-3,5-dinitrobenzoato-$\kappa^3O^1:O^{1'}:O^3$)(μ_2-hydroxido-$\kappa^2O:O$)copper(II)]

B. Sinha, G. C. Dey, B. Sarkar, A. Roy, Seik Weng Ng and Edward R. T. Tiekink

1. Chemical context

2. Structural commentary

The title complex was synthesised employing hydrothermal methods, and X-ray crystallography revealed it to be three-dimensional. The crystallographic asymmetric unit comprises a Cu^{II} cation, and 3,5-dinitrobenzoate and hydroxide anions, Fig. 1. Zigzag rows of Cu^{II} ions are aligned along the *c* axis (glide symmetry) with pairs of Cu^{II} ions being bridged by a hydroxide and two O atoms of the carboxylate ligand leading to chains of six-membered rings. Neighbouring chains are linked *via* Cu—O(nitro) bonds, which are longer than the remaining Cu—O bonds, Table 1. The resulting O_5 donor set defines an axially distorted square pyramidal coordination geometry, with the nitro-O atom in the axial position, as quantified by the value of τ = 0.01 which compares to the τ values of 0.0 and 1.0 for ideal square pyramidal and trigonal bipyramidal geometries, respectively (Addison *et al.*, 1984). Additional stability to the architecture is provided by bifurcated O—H···O(nitro) hydrogen bonds, Table 2.

Similar strings of Cu(μ_2-carboxylate)(μ_2-hydroxyl)Cu of varying dimensionality have been noted in other Cu^{II} structures (*e.g.* Chen *et al.*, 2006; You *et al.*, 2005; Xiao *et al.*, 2006).

3. Supramolecular features

4. Database survey

5. Synthesis and crystallization

To a pulverised mixture of 3,5-dinitrobenzoic acid (0.1688 g), $Cu(NO_3)_2.3H_2O$ (0.1932 g) and melamine (0.1002 g), all obtained from commercial sources in AR grade, distilled water (1.5 ml) was added. The mixture was stirred for 30 min to get a suspension. The reaction mixture was then sealed in a 10 ml Teflon-lined stainless steel autoclave and heated at 423 K for 45 h. The autoclave was subjected to natural cooling (for 5 h) to room temperature. The product containing blue crystals suitable for single crystal X-ray diffraction was collected by filtration and washed with adequate distilled water. The initial pH of the suspension was 5 and there was no apparent change in the pH when the reaction was over. The blue product was not formed in the absence of melamine which suggests that melamine acted as a base in this reaction. The product decomposed with explosion with green flashes above 553 K.

6. Refinement

The H atoms were geometrically placed (O—H = 0.84 Å and C—H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(O, C).

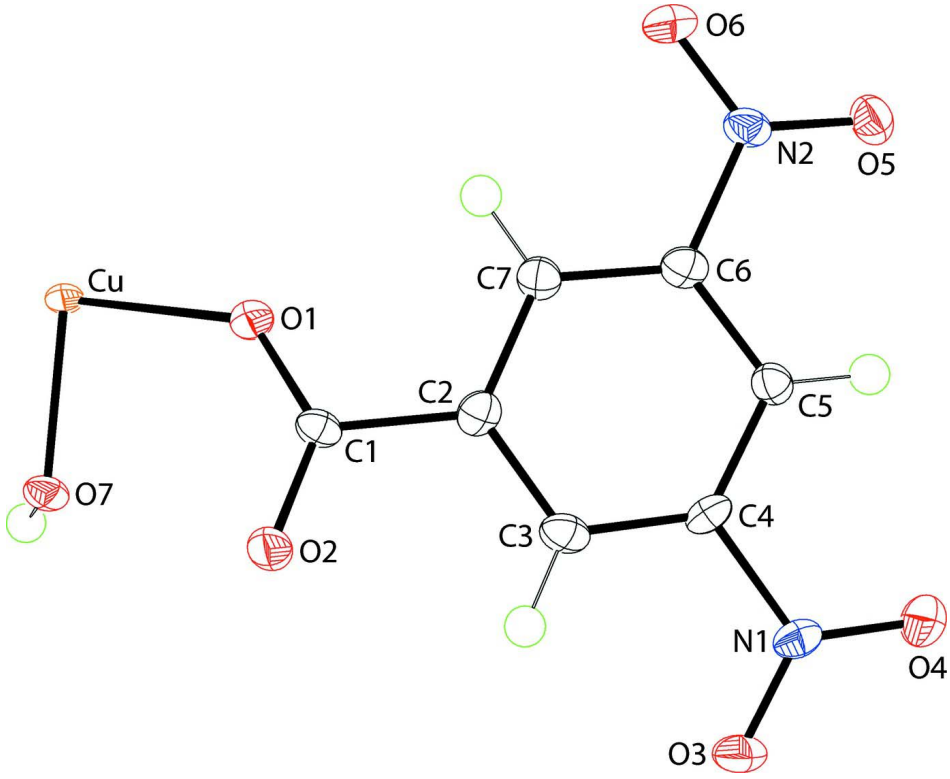

Figure 1

The asymmetric unit of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

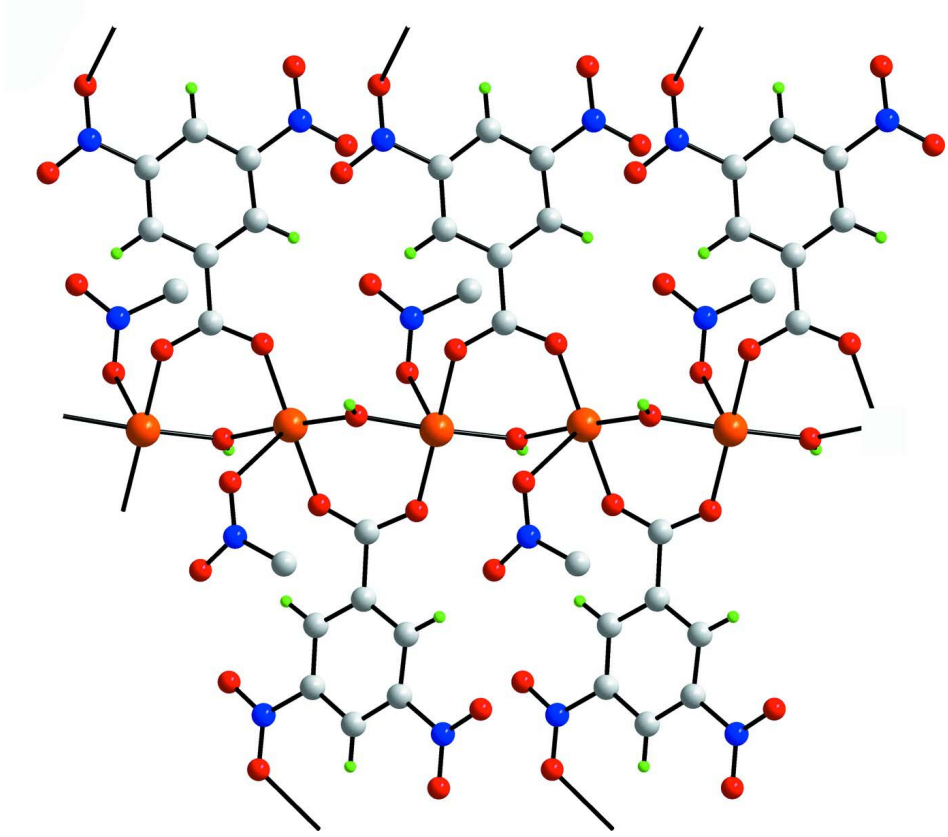

Figure 2

A view approximately normal to the zigzag chain along the *c* axis in the title compound. The coordinating nitro groups from carboxylates belong to other chains are shown as "O_2NC", for reasons of clarity.

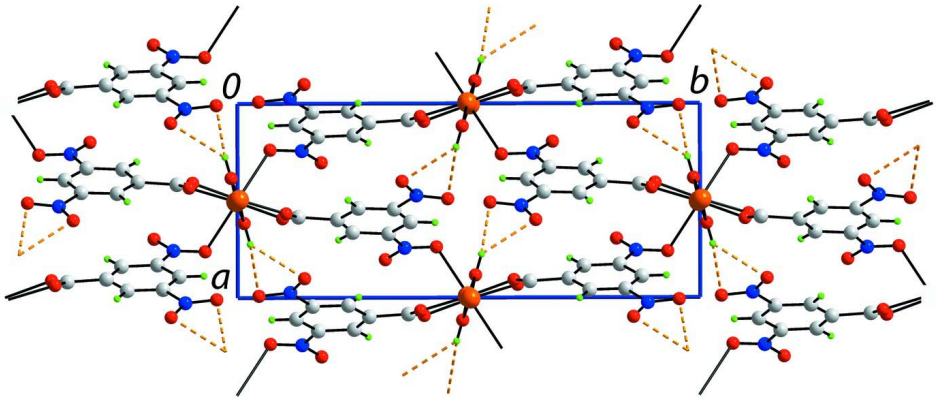

Figure 3

A view of the unit-cell contents of the title compound in projection down the *c* axis, the axis along which the zigzag chains are propagated. The O—H···O hydrogen bonds are shown as orange dashed lines.

Poly[(μ_3-3,5-dinitrobenzoato-$\kappa^3O^1:O^{1'}:O^3$)(μ_2-hydroxido-$\kappa^2O:O$)copper(II)]

Crystal data

$[Cu(C_7H_3N_2O_6)(OH)]$	$F(000) = 580$
$M_r = 291.66$	$D_x = 2.183$ Mg m^{-3}
Orthorhombic, $Pna2_1$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Hall symbol: P 2c -2n	Cell parameters from 2719 reflections
$a = 7.4665$ (2) Å	$\theta = 5.0$–$74.1°$
$b = 17.7858$ (5) Å	$\mu = 3.87$ mm^{-1}
$c = 6.6821$ (2) Å	$T = 100$ K
$V = 887.37$ (4) Å^3	Prism, blue
$Z = 4$	0.25 × 0.20 × 0.15 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector	$T_{min} = 0.873$, $T_{max} = 1.000$
Radiation source: SuperNova (Cu) X-ray Source	3156 measured reflections
Mirror monochromator	1324 independent reflections
Detector resolution: 10.4041 pixels mm^{-1}	1318 reflections with $I > 2\sigma(I)$
ω scan	$R_{int} = 0.017$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)	$\theta_{max} = 74.3°$, $\theta_{min} = 5.0°$
	$h = -6\rightarrow9$
	$k = -20\rightarrow21$
	$l = -7\rightarrow8$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 0.2234P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.077$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.45$ e Å^{-3}
1324 reflections	$\Delta\rho_{min} = -0.67$ e Å^{-3}
155 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.0078 (6)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 360 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.06 (5)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu	0.00521 (5)	0.502896 (17)	0.50002 (17)	0.00920 (17)

O1	0.0918 (2)	0.40286 (10)	0.5811 (3)	0.0146 (4)
O2	0.0673 (3)	0.39533 (9)	0.9179 (3)	0.0136 (4)
O3	−0.0991 (3)	0.14441 (11)	1.1700 (3)	0.0155 (4)
O4	−0.0088 (2)	0.04569 (11)	1.0096 (4)	0.0186 (4)
O5	0.2389 (2)	0.07033 (9)	0.3473 (3)	0.0141 (4)
O6	0.3041 (2)	0.18099 (10)	0.2336 (3)	0.0187 (4)
O7	−0.1161 (2)	0.51396 (9)	0.7481 (3)	0.0105 (4)
H1	−0.2242	0.5270	0.7463	0.016*
N1	−0.0260 (3)	0.11347 (12)	1.0269 (4)	0.0124 (5)
N2	0.2439 (3)	0.13903 (11)	0.3632 (3)	0.0119 (4)
C1	0.0847 (3)	0.36866 (12)	0.7455 (4)	0.0099 (4)
C2	0.0984 (3)	0.28424 (13)	0.7318 (4)	0.0110 (5)
C3	0.0397 (4)	0.23927 (14)	0.8891 (4)	0.0121 (5)
H3	−0.0025	0.2611	1.0100	0.014*
C4	0.0445 (4)	0.16166 (14)	0.8649 (4)	0.0109 (5)
C5	0.1101 (4)	0.12656 (13)	0.6959 (4)	0.0108 (5)
H5	0.1135	0.0734	0.6839	0.013*
C6	0.1710 (3)	0.17364 (13)	0.5442 (4)	0.0113 (5)
C7	0.1637 (3)	0.25149 (13)	0.5565 (4)	0.0111 (5)
H7	0.2024	0.2819	0.4478	0.013*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0143 (3)	0.0092 (2)	0.0042 (3)	0.00052 (10)	0.00062 (13)	0.00047 (15)
O1	0.0228 (10)	0.0118 (8)	0.0092 (9)	0.0025 (6)	0.0030 (7)	0.0015 (7)
O2	0.0210 (10)	0.0118 (8)	0.0081 (9)	0.0024 (7)	−0.0017 (7)	−0.0004 (7)
O3	0.0177 (9)	0.0182 (9)	0.0105 (9)	−0.0005 (8)	0.0047 (7)	−0.0002 (7)
O4	0.0268 (11)	0.0112 (8)	0.0179 (10)	−0.0027 (6)	0.0038 (8)	0.0013 (10)
O5	0.0173 (9)	0.0119 (8)	0.0129 (9)	0.0024 (6)	−0.0015 (7)	−0.0019 (7)
O6	0.0258 (10)	0.0180 (9)	0.0122 (9)	−0.0006 (7)	0.0079 (9)	0.0013 (8)
O7	0.0124 (9)	0.0129 (7)	0.0061 (8)	0.0010 (6)	−0.0013 (8)	−0.0012 (8)
N1	0.0134 (10)	0.0153 (10)	0.0085 (12)	0.0000 (8)	−0.0008 (8)	0.0025 (9)
N2	0.0131 (10)	0.0150 (9)	0.0075 (10)	0.0030 (7)	−0.0005 (8)	−0.0006 (8)
C1	0.0092 (10)	0.0126 (11)	0.0080 (11)	0.0015 (8)	−0.0009 (10)	−0.0015 (10)
C2	0.0111 (10)	0.0121 (11)	0.0099 (12)	0.0004 (9)	−0.0028 (11)	0.0014 (11)
C3	0.0124 (11)	0.0158 (13)	0.0080 (12)	0.0018 (9)	−0.0014 (10)	−0.0014 (10)
C4	0.0116 (11)	0.0130 (12)	0.0081 (12)	−0.0019 (9)	−0.0010 (11)	0.0033 (9)
C5	0.0118 (11)	0.0109 (11)	0.0098 (13)	0.0012 (9)	−0.0010 (9)	−0.0007 (9)
C6	0.0113 (11)	0.0144 (10)	0.0081 (13)	0.0010 (8)	−0.0022 (9)	−0.0003 (8)
C7	0.0121 (11)	0.0117 (10)	0.0095 (12)	−0.0004 (9)	−0.0016 (9)	−0.0009 (8)

Geometric parameters (Å, º)

Cu—O1	1.9689 (18)	O7—H1	0.8400
Cu—O7	1.899 (2)	N1—C4	1.478 (3)
Cu—O2^{i}	1.9675 (18)	N2—C6	1.462 (3)
Cu—O5^{ii}	2.5871 (18)	C1—C2	1.508 (3)
Cu—O7^{i}	1.900 (2)	C2—C3	1.392 (4)
O1—C1	1.257 (4)	C2—C7	1.396 (4)

O2—C1	1.252 (3)	C3—C4	1.390 (4)
O2—Cu^{iii}	1.9675 (18)	C3—H3	0.9500
O3—N1	1.231 (3)	C4—C5	1.380 (4)
O4—N1	1.218 (3)	C5—C6	1.391 (3)
O5—N2	1.227 (3)	C5—H5	0.9500
O6—N2	1.228 (3)	C6—C7	1.388 (3)
O7—Cu^{iii}	1.900 (2)	C7—H7	0.9500
O7—Cu—O7^{i}	176.03 (4)	O2—C1—O1	128.7 (2)
O7—Cu—O2^{i}	90.98 (8)	O2—C1—C2	116.1 (2)
O7^{i}—Cu—O2^{i}	91.02 (9)	O1—C1—C2	115.2 (2)
O7—Cu—O1	90.57 (9)	C3—C2—C7	120.3 (2)
O7^{i}—Cu—O1	87.60 (8)	C3—C2—C1	120.3 (2)
O2^{i}—Cu—O1	176.81 (9)	C7—C2—C1	119.4 (2)
O7—Cu—O5^{ii}	91.71 (7)	C4—C3—C2	118.3 (2)
O7^{i}—Cu—O5^{ii}	84.60 (8)	C4—C3—H3	120.8
O2^{i}—Cu—O5^{ii}	98.13 (7)	C2—C3—H3	120.8
O1—Cu—O5^{ii}	84.60 (7)	C5—C4—C3	123.6 (2)
C1—O1—Cu	131.60 (17)	C5—C4—N1	117.6 (2)
C1—O2—Cu^{iii}	129.32 (16)	C3—C4—N1	118.8 (2)
Cu—O7—Cu^{iii}	123.32 (10)	C4—C5—C6	116.1 (2)
Cu—O7—H1	118.3	C4—C5—H5	122.0
Cu^{iii}—O7—H1	118.3	C6—C5—H5	122.0
O4—N1—O3	124.3 (2)	C7—C6—C5	123.0 (2)
O4—N1—C4	117.8 (2)	C7—C6—N2	118.9 (2)
O3—N1—C4	117.9 (2)	C5—C6—N2	118.1 (2)
O5—N2—O6	123.7 (2)	C6—C7—C2	118.6 (2)
O5—N2—C6	118.7 (2)	C6—C7—H7	120.7
O6—N2—C6	117.62 (19)	C2—C7—H7	120.7
O7—Cu—O1—C1	−8.5 (2)	O4—N1—C4—C5	6.0 (3)
O7^{i}—Cu—O1—C1	175.0 (2)	O3—N1—C4—C5	−173.7 (2)
O2^{i}—Cu—O7—Cu^{iii}	−127.01 (11)	O4—N1—C4—C3	−174.7 (2)
O1—Cu—O7—Cu^{iii}	50.20 (11)	O3—N1—C4—C3	5.7 (4)
Cu^{iii}—O2—C1—O1	14.1 (4)	C3—C4—C5—C6	−0.9 (4)
Cu^{iii}—O2—C1—C2	−165.63 (15)	N1—C4—C5—C6	178.3 (2)
Cu—O1—C1—O2	−22.7 (4)	C4—C5—C6—C7	−1.5 (3)
Cu—O1—C1—C2	156.98 (16)	C4—C5—C6—N2	179.2 (2)
O2—C1—C2—C3	19.2 (3)	O5—N2—C6—C7	−175.1 (2)
O1—C1—C2—C3	−160.6 (2)	O6—N2—C6—C7	3.6 (3)
O2—C1—C2—C7	−163.4 (2)	O5—N2—C6—C5	4.2 (3)
O1—C1—C2—C7	16.8 (3)	O6—N2—C6—C5	−177.0 (2)
C7—C2—C3—C4	−1.3 (4)	C5—C6—C7—C2	2.4 (3)
C1—C2—C3—C4	176.0 (2)	N2—C6—C7—C2	−178.3 (2)
C2—C3—C4—C5	2.3 (4)	C3—C2—C7—C6	−0.9 (3)
C2—C3—C4—N1	−176.9 (2)	C1—C2—C7—C6	−178.3 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H1···O3^{iv}	0.84	2.52	3.190 (3)	137
O7—H1···O4^{iv}	0.84	2.57	3.271 (2)	142

Symmetry code: (iv) $-x-1/2, y+1/2, z-1/2$.