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catena-Poly[[(1,10-phenanthroline)-copper(II)]-*μ*-oxalato]

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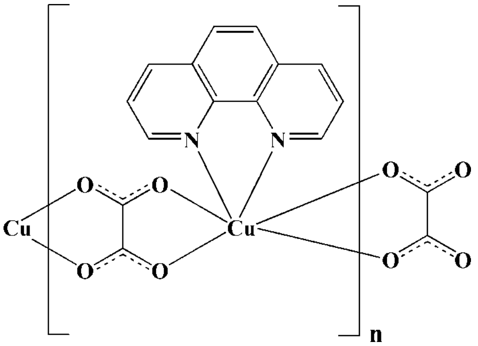
Key indicators: single-crystal X-ray study; *T* = 298 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.024; *wR* factor = 0.059; data-to-parameter ratio = 13.8.

In the title coordination polymer, $[Cu(C_2O_4)(C_{12}H_8N_2)]_n$, the Cu^{II} atom is six-coordinated by four O atoms from two oxalate ligands and two N atoms from one 1,10-phenanthroline (phen) ligand in a distorted octahedral coordination geometry. The oxalate anions act as bis-bidentate ligands, bridging the Cu–phen units in zigzag chains extending parallel to [100]. Interchain C—H⋯O hydrogen bonding and π–π stacking interactions [centroid–centroid distance = 3.7439 (17) Å] assemble neighboring chains, forming a three-dimensional supramolecular network.

Related literature

For the topologies and potential applications as functional materials of metal coordination polymers, see: Benneli & Gatteschi (2002); Qin *et al.* (2005); Qiu *et al.* (2007).



Experimental

Crystal data

$[Cu(C_2O_4)(C_{12}H_8N_2)]$
M_r = 331.76
Orthorhombic, $Pna2_1$
a = 9.1445 (8) Å
b = 10.1443 (9) Å
c = 13.3294 (11) Å
V = 1236.50 (18) Å^3
Z = 4
Mo *Kα* radiation
μ = 1.78 mm^{-1}
T = 298 K
0.42 × 0.35 × 0.29 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008)
T_{min} = 0.544, T_{max} = 0.612
6811 measured reflections
2618 independent reflections
2373 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.059
S = 1.04
2618 reflections
190 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Absolute structure: Flack (1983), 1217 Friedel pairs
Flack parameter: 0.019 (14)

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C11—H11⋯O4^{i}	0.93	2.51	3.416 (4)	166
C9—H9⋯O1^{ii}	0.93	2.49	3.160 (3)	129
C2—H2⋯O2^{iii}	0.93	2.52	3.136 (3)	124
C1—H1⋯O4^{iv}	0.93	2.56	3.072 (3)	115

Symmetry codes: (i) $-x+\frac{5}{2}, y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{5}{2}, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2304).

References

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supporting information

Acta Cryst. (2010). E**66**, m1229 [doi:10.1107/S1600536810035440]

catena-Poly[[(1,10-phenanthroline)copper(II)]-μ-oxalato]

Jun Wang, Yong Hou and Zhi-li Fang

S1. Comment

The design and construction of metal coordination polymers based on metal ions and multifunctional bridging ligands is of great interest due to their intriguing topologies and potential applications as functional materials (Benneli & Gatteschi, 2002; Qiu *et al.*, 2007). Copper, with its variable coordination numbers and flexible coordination geometry, provides unique opportunities for the discovery of unusual networks in this interesting and challenging field (Qin *et al.*, 2005). We chose oxalate ligands as organic spacers since this rigid molecule has proven to be able to establish a bridge between metal centers. Herein, we present the structure of the title compound, $[Cu(C_2O_4)(C_{12}H_8N_2)]_n$.

The Cu^{II} atom exhibits a distorted octahedral configuration coordinated by four oxygen atoms from two oxalate ligands (Cu—O = 1.9753 (18)-2.3135 (18) Å) and two nitrogen atoms from one 1,10-phenanthroline ligand (Cu—N = 2.024 (2) and 2.049 (2) Å) (Fig. 1). The oxalate ligands bridge adjacent Cu-phen units to form a one-dimensional zigzag chain along the a-axis of the unit cell. The Cu—Cu separation is 5.529 (2) Å. Interchain π-π stacking interactions between phen ligands in neighboring chainslead to the formation of sheets of connected chains in the *ab*-plane. The centroid to centroid distances between neighboring 1,10-phenanthroline ligands is 3.7439 (17) Å [ring (C4-C9) to ring (N2, C1 to C5) (symmetry code: $-1/2+x$, $3/2-y$, z)]. C–H···O hydrogen bonds interconnect these sheets to extend to a three-dimensional supramolecular network motif (Table 1; Fig. 2).

S2. Experimental

A sample of cupric acetate (0.0399 g, 0.20 mmol), oxalic acid (0.1015 g, 0.50 mmol), 1,10-phenanthroline (0.2523 g, 0.50 mmol), were added to water (10 ml). The resultant mixture was sealed in a 25 ml stainless steel reactor with a Teflon liner and kept under autogenous pressure at 413 K for 78 h, and then cooled to room temperature at a rate of 0.5 K/min. Colorless blocky crystals of the title compound suitable for single-crystal X-ray diffraction analyses formed in a yield of approximately 65%.

S3. Refinement

All H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93 Å, and with U_{iso}(H) = 1.2 (C).

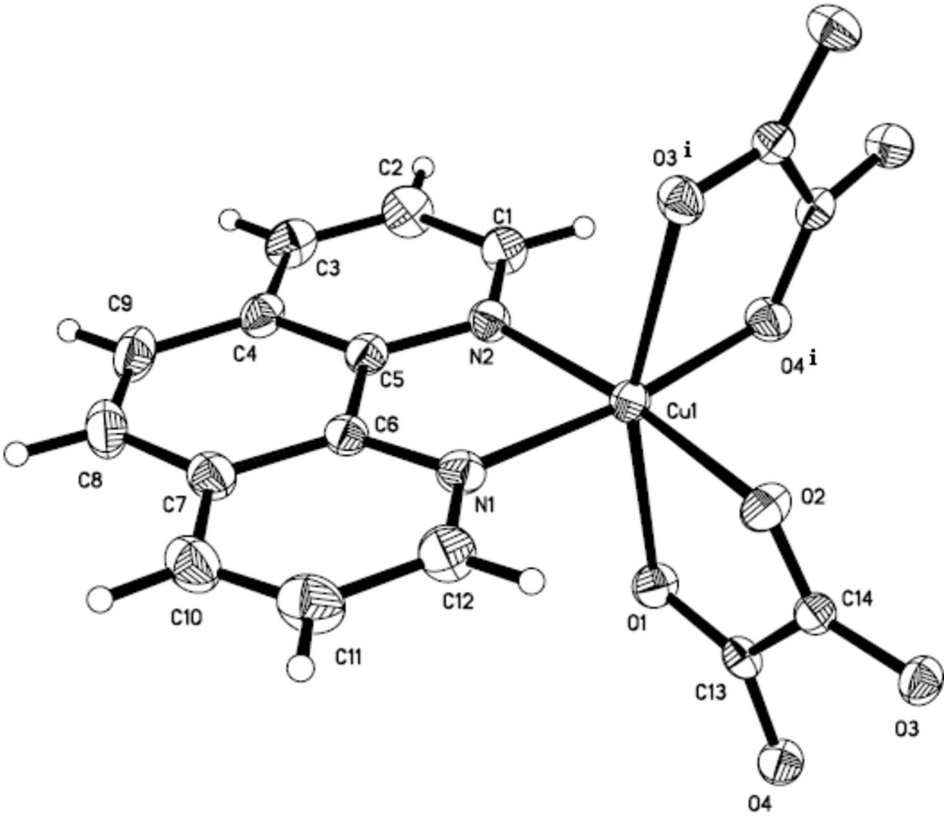

Figure 1

ORTEP represention of atom numbering diagram for the title complex, showing 30% probability displacement ellipsoids. Symmetry code: (i) –1/2 + *x*, 2.5–*y*, *z*.

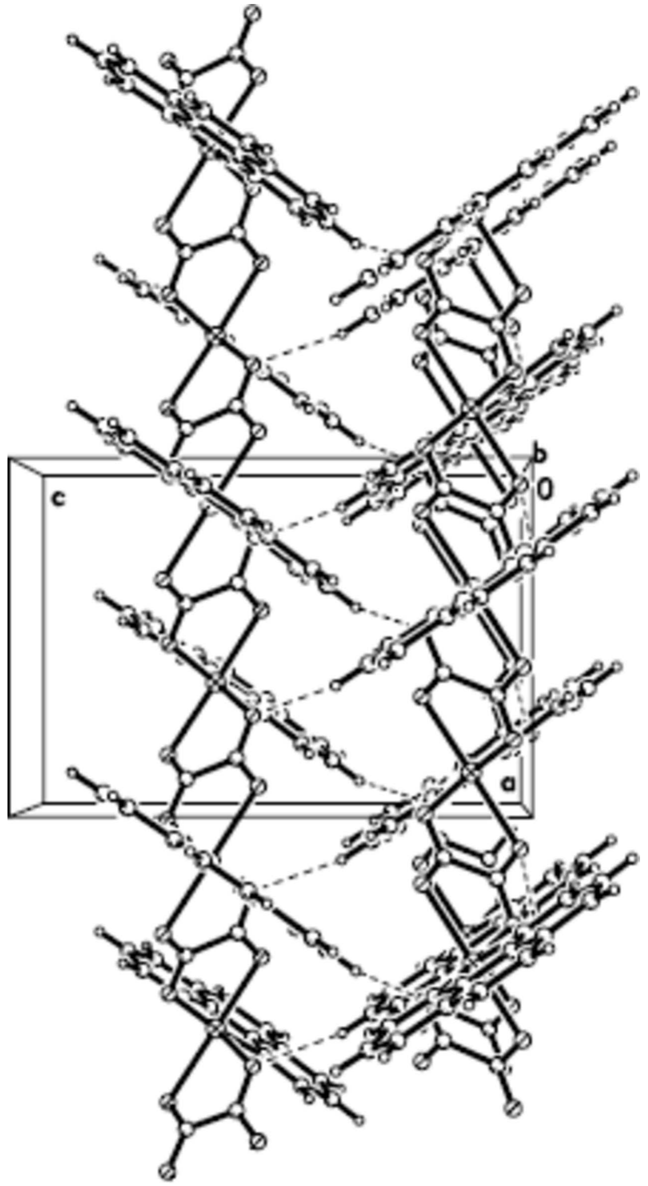

Figure 2

View of the three-dimensional structure of the title compound.

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Crystal data

$[Cu(C_2O_4)(C_{12}H_8N_2)]$
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Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
$a = 9.1445$ (8) Å
$b = 10.1443$ (9) Å
$c = 13.3294$ (11) Å
$V = 1236.50$ (18) Å^3
$Z = 4$

$F(000) = 668$
$D_x = 1.782$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2618 reflections
$\theta = 2.5$–$27.0°$
$\mu = 1.78$ mm^{-1}
$T = 298$ K
Block, blue
0.42 × 0.35 × 0.29 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008)
$T_{\min} = 0.544$, $T_{\max} = 0.612$

6811 measured reflections
2618 independent reflections
2373 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$
$\theta_{\max} = 27.0°$, $\theta_{\min} = 2.5°$
$h = -8 \rightarrow 11$
$k = -10 \rightarrow 12$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.04$
2618 reflections
190 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Absolute structure: Flack (1983), 1217 Friedel pairs
Absolute structure parameter: 0.019 (14)

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}
C1	0.6938 (3)	0.9764 (3)	−0.04988 (19)	0.0407 (6)
H1	0.6652	1.0617	−0.0662	0.049*
Cu1	0.87241 (3)	1.09675 (2)	0.11815 (4)	0.03062 (9)
N1	0.9474 (2)	0.9310 (2)	0.18929 (17)	0.0352 (5)
O1	1.0814 (2)	1.12990 (18)	0.02682 (14)	0.0377 (4)
C2	0.6422 (3)	0.8724 (3)	−0.1095 (2)	0.0486 (7)
H2	0.5818	0.8883	−0.1643	0.058*
N2	0.7802 (2)	0.9598 (2)	0.02762 (16)	0.0325 (4)
O2	0.98329 (19)	1.21773 (18)	0.20589 (13)	0.0377 (4)
C3	0.6829 (3)	0.7475 (3)	−0.0849 (2)	0.0472 (7)
H3	0.6506	0.6770	−0.1237	0.057*
O3	1.1635 (2)	1.36277 (17)	0.21108 (14)	0.0358 (4)
C4	0.7727 (3)	0.7242 (2)	−0.0022 (2)	0.0386 (6)
O4	1.2795 (2)	1.25638 (18)	0.04136 (14)	0.0376 (4)
C5	0.8190 (3)	0.8351 (2)	0.05270 (19)	0.0321 (5)

C6	0.9086 (2)	0.8194 (2)	0.13957 (17)	0.0307 (6)
C7	0.9518 (3)	0.6918 (3)	0.1703 (2)	0.0404 (6)
C8	0.9027 (3)	0.5816 (2)	0.1130 (4)	0.0500 (7)
H8	0.9293	0.4971	0.1330	0.060*
C9	0.8186 (4)	0.5967 (2)	0.0306 (3)	0.0485 (7)
H9	0.7899	0.5226	−0.0055	0.058*
C10	1.0386 (3)	0.6850 (3)	0.2567 (2)	0.0498 (7)
H10	1.0723	0.6038	0.2794	0.060*
C11	1.0740 (4)	0.7970 (3)	0.3077 (3)	0.0555 (8)
H11	1.1295	0.7922	0.3660	0.067*
C12	1.0266 (3)	0.9184 (3)	0.2720 (2)	0.0471 (7)
H12	1.0515	0.9940	0.3076	0.056*
C13	1.1578 (3)	1.2130 (2)	0.07154 (19)	0.0303 (5)
C14	1.0979 (3)	1.2700 (2)	0.17167 (19)	0.0288 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0439 (15)	0.0420 (14)	0.0362 (14)	0.0018 (12)	−0.0088 (12)	−0.0036 (12)
Cu1	0.03102 (14)	0.02964 (14)	0.03119 (13)	−0.00071 (10)	−0.00153 (13)	−0.00414 (16)
N1	0.0315 (11)	0.0393 (11)	0.0347 (12)	0.0005 (9)	−0.0041 (9)	−0.0007 (9)
O1	0.0370 (10)	0.0409 (9)	0.0350 (10)	−0.0020 (8)	0.0025 (8)	−0.0107 (8)
C2	0.0555 (19)	0.0558 (17)	0.0346 (15)	0.0010 (14)	−0.0120 (13)	−0.0089 (13)
N2	0.0336 (10)	0.0323 (10)	0.0317 (11)	0.0008 (8)	−0.0013 (9)	−0.0039 (9)
O2	0.0365 (11)	0.0433 (10)	0.0335 (10)	−0.0101 (8)	0.0092 (8)	−0.0118 (9)
C3	0.0500 (18)	0.0539 (17)	0.0376 (16)	−0.0090 (14)	−0.0026 (14)	−0.0157 (13)
O3	0.0382 (10)	0.0329 (9)	0.0361 (10)	−0.0043 (8)	0.0007 (8)	−0.0064 (8)
C4	0.0393 (14)	0.0370 (13)	0.0395 (15)	−0.0068 (11)	0.0064 (11)	−0.0096 (12)
O4	0.0363 (10)	0.0388 (9)	0.0377 (10)	−0.0026 (8)	0.0102 (8)	−0.0030 (8)
C5	0.0320 (13)	0.0337 (13)	0.0307 (13)	−0.0018 (11)	0.0058 (11)	−0.0035 (10)
C6	0.0288 (12)	0.0328 (12)	0.0305 (16)	0.0004 (9)	0.0055 (9)	−0.0016 (9)
C7	0.0375 (14)	0.0414 (15)	0.0424 (15)	0.0040 (12)	0.0059 (12)	0.0067 (12)
C8	0.0599 (17)	0.0306 (12)	0.0593 (18)	0.0031 (10)	0.011 (2)	0.0032 (18)
C9	0.0581 (18)	0.0317 (15)	0.056 (2)	−0.0092 (12)	0.0074 (16)	−0.0072 (13)
C10	0.0491 (18)	0.0495 (18)	0.0509 (19)	0.0092 (13)	0.0012 (14)	0.0111 (14)
C11	0.0519 (19)	0.068 (2)	0.0465 (19)	0.0056 (17)	−0.0099 (15)	0.0107 (17)
C12	0.0499 (17)	0.0496 (16)	0.0417 (16)	0.0011 (13)	−0.0124 (13)	−0.0052 (13)
C13	0.0327 (13)	0.0285 (12)	0.0296 (12)	0.0062 (10)	−0.0010 (11)	0.0017 (10)
C14	0.0293 (12)	0.0297 (12)	0.0274 (12)	0.0011 (10)	−0.0030 (10)	−0.0022 (11)

Geometric parameters (Å, º)

C1—N2	1.311 (3)	O3—Cu1$^{\rm ii}$	2.3135 (18)
C1—C2	1.403 (4)	C4—C5	1.407 (3)
C1—H1	0.9300	C4—C9	1.428 (4)
Cu1—O2	1.9753 (18)	O4—C13	1.263 (3)
Cu1—O4$^{\rm i}$	1.9973 (19)	O4—Cu1$^{\rm ii}$	1.9973 (19)
Cu1—N2	2.024 (2)	C5—C6	1.428 (3)

Cu1—N1	2.049 (2)	C6—C7	1.414 (3)
Cu1—O1	2.2909 (19)	C7—C10	1.401 (4)
Cu1—O3^{i}	2.3135 (18)	C7—C8	1.426 (5)
N1—C12	1.325 (4)	C8—C9	1.350 (6)
N1—C6	1.359 (3)	C8—H8	0.9300
O1—C13	1.247 (3)	C9—H9	0.9300
C2—C3	1.360 (5)	C10—C11	1.363 (4)
C2—H2	0.9300	C10—H10	0.9300
N2—C5	1.356 (3)	C11—C12	1.390 (4)
O2—C14	1.260 (3)	C11—H11	0.9300
C3—C4	1.395 (4)	C12—H12	0.9300
C3—H3	0.9300	C13—C14	1.554 (3)
O3—C14	1.234 (3)		

N2—C1—C2	123.5 (2)	C3—C4—C9	124.7 (3)
N2—C1—H1	118.3	C5—C4—C9	118.4 (3)
C2—C1—H1	118.3	C13—O4—Cu1^{ii}	118.13 (17)
O2—Cu1—O4^{i}	93.34 (8)	N2—C5—C4	122.6 (2)
O2—Cu1—N2	173.31 (8)	N2—C5—C6	117.0 (2)
O4^{i}—Cu1—N2	91.68 (9)	C4—C5—C6	120.4 (2)
O2—Cu1—N1	93.68 (8)	N1—C6—C7	123.3 (2)
O4^{i}—Cu1—N1	172.68 (8)	N1—C6—C5	116.9 (2)
N2—Cu1—N1	81.49 (9)	C7—C6—C5	119.8 (2)
O2—Cu1—O1	78.18 (7)	C10—C7—C6	116.2 (2)
O4^{i}—Cu1—O1	88.46 (7)	C10—C7—C8	125.5 (3)
N2—Cu1—O1	97.55 (7)	C6—C7—C8	118.3 (3)
N1—Cu1—O1	95.01 (8)	C9—C8—C7	121.7 (3)
O2—Cu1—O3^{i}	89.80 (7)	C9—C8—H8	119.1
O4^{i}—Cu1—O3^{i}	77.92 (7)	C7—C8—H8	119.1
N2—Cu1—O3^{i}	95.57 (7)	C8—C9—C4	121.3 (3)
N1—Cu1—O3^{i}	100.03 (8)	C8—C9—H9	119.3
O1—Cu1—O3^{i}	161.33 (6)	C4—C9—H9	119.3
C12—N1—C6	117.9 (2)	C11—C10—C7	120.2 (3)
C12—N1—Cu1	130.30 (19)	C11—C10—H10	119.9
C6—N1—Cu1	111.77 (16)	C7—C10—H10	119.9
C13—O1—Cu1	108.21 (16)	C10—C11—C12	119.6 (3)
C3—C2—C1	118.2 (3)	C10—C11—H11	120.2
C3—C2—H2	120.9	C12—C11—H11	120.2
C1—C2—H2	120.9	N1—C12—C11	122.7 (3)
C1—N2—C5	118.1 (2)	N1—C12—H12	118.6
C1—N2—Cu1	129.22 (18)	C11—C12—H12	118.6
C5—N2—Cu1	112.62 (16)	O1—C13—O4	125.2 (2)
C14—O2—Cu1	118.30 (16)	O1—C13—C14	117.7 (2)
C2—C3—C4	120.6 (3)	O4—C13—C14	117.1 (2)
C2—C3—H3	119.7	O3—C14—O2	124.9 (2)
C4—C3—H3	119.7	O3—C14—C13	118.5 (2)

C14—O3—Cu1^{ii}	108.00 (16)	O2—C14—C13	116.6 (2)
C3—C4—C5	116.9 (2)		

Symmetry codes: (i) *x*−1/2, −*y*+5/2, *z*; (ii) *x*+1/2, −*y*+5/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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Symmetry codes: (i) *x*−1/2, −*y*+5/2, *z*; (iii) −*x*+5/2, *y*−1/2, *z*+1/2; (iv) *x*−1/2, −*y*+3/2, *z*; (v) −*x*+3/2, *y*−1/2, *z*−1/2.