

Poly[[$(\mu_3$ -5,6-dicarboxybicyclo[2.2.2]oct-7-ene-2,3-dicarboxylato)(1,10-phenanthroline)copper(II)] monohydrate]

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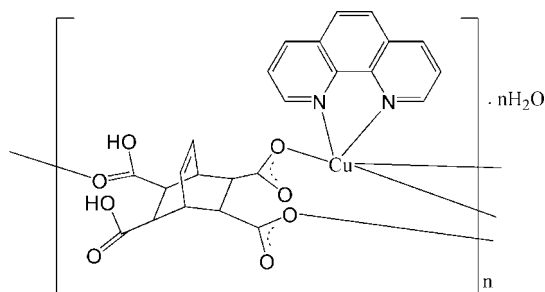
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Received 13 November 2008; accepted 15 November 2008

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.065; data-to-parameter ratio = 13.7.

In the title compound, $\{[\text{Cu}(\text{C}_{12}\text{H}_{10}\text{O}_8)(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}\}_n$, the Cu^{II} ion is five-coordinated by two N atoms from one phenanthroline ligand and three O atoms from three different H_2L^{2-} anions (H_4L is bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid) in a distorted square-pyramidal geometry. Each H_2L^{2-} ion bridges three Cu^{II} atoms to form a zigzag sheet parallel to the ab plane. The crystal structure is consolidated by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

Related literature

 For general background, see: Yang *et al.* (2008).


Experimental

Crystal data

$[\text{Cu}(\text{C}_{12}\text{H}_{10}\text{O}_8)(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$
 $M_r = 543.96$
 Monoclinic, $P2_1$
 $a = 6.5900$ (4) Å
 $b = 15.1650$ (8) Å
 $c = 10.7490$ (6) Å
 $\beta = 95.244$ (9)°

$V = 1069.73$ (10) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.08$ mm⁻¹
 $T = 293$ (2) K
 $0.33 \times 0.21 \times 0.20$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.696$, $T_{\text{max}} = 0.803$

6580 measured reflections
 4555 independent reflections
 4343 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.065$
 $S = 1.04$
 4555 reflections
 333 parameters
 2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³
 Absolute structure: Flack (1983), 1914 Friedel pairs
 Flack parameter: 0.008 (8)

Table 1

Selected bond lengths (Å).

N1—Cu1	2.0072 (17)	Cu1—O3 ⁱ	1.9355 (15)
N2—Cu1	2.0119 (19)	Cu1—O7 ⁱⁱ	2.3398 (18)
O2—Cu1	1.9640 (15)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O5—H5 [·] ··O1W	0.82	1.84	2.567 (2)	148
O8—H8 [·] ··O2 ⁱⁱⁱ	0.82	1.79	2.594 (2)	166
O1W—HW11 [·] ··O4 ^{iv}	0.82 (3)	1.97 (3)	2.777 (3)	167 (3)
O1W—HW12 [·] ··O1 ^v	0.82 (2)	2.05 (3)	2.763 (3)	145 (4)

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL-Plus (Sheldrick, 2008); software used to prepare material for publication: SHELXTL-Plus (Sheldrick, 2008).

The authors thank the Science Foundation for Young Teachers of Northeast Normal University (grant Nos. 20080305 and 20080304) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2718).

References

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supplementary materials

Acta Cryst. (2008). E64, m1590 [doi:10.1107/S1600536808037999]

Poly[[$(\mu_3$ -5,6-dicarboxybicyclo[2.2.2]oct-7-ene-2,3-dicarboxylato)(1,10-phenanthroline)copper(II)] monohydrate]

Y.-Y. Liu, Y.-J. Zhuo, X.-Q. Li and J.-C. Ma

Comment

Coordination polymers based on poly(carboxylic acids) have been investigated in the area of solid state and material science (Yang *et al.*, 2008). We selected bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid (H_4L) as a poly(carboxylic acid) ligand and phenanthroline (phen) as a secondary ligand, generating a new coordination polymer, $[Cu(phen)(H_2L)] \cdot H_2O$, which is reported here.

In the title compound, each Cu^{II} atom is five-coordinated by two N atoms from one phen ligand, and three O atoms from three different H_2L^{2-} anions in a distorted square-pyramidal geometry (Fig. 1 and Table 1). Each H_2L^{2-} bridges three Cu^{II} atoms to form a two-dimensional layer structure (Fig. 2). The O—H \cdots O hydrogen bonds (Table 2) further consolidate the crystal structure.

Experimental

A mixture of H_4L (0.5 mmol), phen (0.5 mmol), NaOH (1 mmol) and $CuCl_2 \cdot 2H_2O$ (0.5 mmol) was suspended in deionized water (12 ml) and sealed in a 20-ml Teflon-lined autoclave. The mixture was heated at 373 K for 7 d and then the autoclave was slowly cooled to room temperature. The grown single crystals were collected, washed with deionized water and dried.

Refinement

H atoms on C atoms were generated geometrically and refined as riding atoms with C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the water molecules were located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å and with $U_{iso}(H) = 1.2U_{eq}(O)$.

Figures

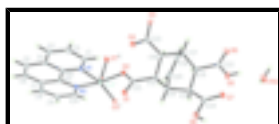


Fig. 1. Part of the polymeric structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (i) $x - 1, y, z$; (ii) $2 - x, y - 1/2, 2 - z$.

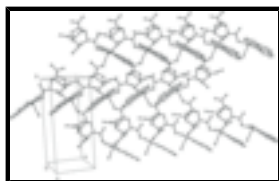


Fig. 2. View of a zigzag sheet structure in the title compound.

Poly[[$(\mu_3$ -5,6-dicarboxybicyclo[2.2.2]oct-7-ene-2,3-dicarboxylato)(1,10-phenanthroline)copper(II)] monohydrate]

Crystal data

$[\text{Cu}(\text{C}_{12}\text{H}_{10}\text{O}_8)(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$	$F_{000} = 558$
$M_r = 543.96$	$D_x = 1.689 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
Hall symbol: P 2yb	$\lambda = 0.71069 \text{ \AA}$
$a = 6.5900 (4) \text{ \AA}$	Cell parameters from 4555 reflections
$b = 15.1650 (8) \text{ \AA}$	$\theta = 1.1\text{--}28.4^\circ$
$c = 10.7490 (6) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$\beta = 95.244 (9)^\circ$	$T = 293 \text{ K}$
$V = 1069.73 (10) \text{ \AA}^3$	Block, blue
$Z = 2$	$0.33 \times 0.21 \times 0.20 \text{ mm}$

Data collection

Bruker APEX CCD area-detector diffractometer	4555 independent reflections
Radiation source: fine-focus sealed tube	4343 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.022$
$T = 293 \text{ K}$	$\theta_{\text{max}} = 28.4^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.696$, $T_{\text{max}} = 0.803$	$k = -19 \rightarrow 17$
6580 measured reflections	$l = -6 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4555 reflections	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
333 parameters	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
2 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1914 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.008 (8)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8692 (4)	0.81993 (17)	0.5050 (2)	0.0327 (5)
H1	0.9536	0.8445	0.5700	0.039*
C2	0.9222 (4)	0.82867 (19)	0.3826 (2)	0.0382 (6)
H2	1.0408	0.8583	0.3669	0.046*
C3	0.7992 (4)	0.79351 (17)	0.2862 (2)	0.0362 (6)
H3	0.8341	0.7990	0.2047	0.043*
C4	0.6199 (3)	0.74901 (17)	0.31010 (18)	0.0285 (5)
C5	0.4749 (4)	0.71054 (18)	0.2161 (2)	0.0352 (6)
H5A	0.4972	0.7156	0.1322	0.042*
C6	0.3084 (4)	0.66765 (18)	0.2479 (2)	0.0361 (6)
H6	0.2186	0.6434	0.1853	0.043*
C7	0.2660 (4)	0.65841 (16)	0.3763 (2)	0.0291 (5)
C8	0.1009 (4)	0.61105 (18)	0.4178 (2)	0.0364 (6)
H8B	0.0083	0.5828	0.3606	0.044*
C9	0.0779 (4)	0.60707 (19)	0.5428 (2)	0.0377 (6)
H9	-0.0301	0.5758	0.5711	0.045*
C10	0.2174 (4)	0.65023 (17)	0.6279 (2)	0.0329 (5)
H10	0.1995	0.6473	0.7127	0.039*
C11	0.4003 (3)	0.69806 (15)	0.46831 (19)	0.0240 (4)
C12	0.5789 (3)	0.74318 (14)	0.43543 (18)	0.0237 (5)
C13	1.0048 (3)	0.90548 (13)	0.94151 (18)	0.0192 (4)
H13	0.9289	0.8814	1.0080	0.023*
C14	1.0387 (3)	1.00356 (15)	0.97408 (18)	0.0223 (4)
H14	0.9159	1.0382	0.9497	0.027*
C15	1.0971 (3)	1.00950 (14)	1.11723 (18)	0.0220 (4)
H15	0.9782	0.9919	1.1598	0.026*
C16	1.2682 (3)	0.94109 (14)	1.14952 (18)	0.0211 (4)
H16	1.1993	0.8873	1.1736	0.025*
C17	1.3679 (3)	0.91758 (15)	1.02845 (19)	0.0229 (4)
H17	1.4990	0.8879	1.0479	0.027*
C18	1.2122 (3)	0.85576 (14)	0.95247 (18)	0.0203 (4)
H18	1.1978	0.8014	1.0002	0.024*
C19	1.3913 (3)	0.99816 (16)	0.94838 (19)	0.0288 (5)

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H19	1.5166	1.0168	0.9246	0.035*
C20	1.2195 (4)	1.03987 (15)	0.91496 (19)	0.0268 (5)
H20	1.2108	1.0873	0.8600	0.032*
C21	0.8703 (3)	0.88961 (15)	0.82048 (19)	0.0208 (4)
C22	1.2984 (3)	0.83259 (15)	0.82983 (19)	0.0237 (4)
C23	1.4200 (4)	0.96369 (15)	1.2593 (2)	0.0265 (5)
C24	1.1515 (3)	1.10347 (15)	1.1550 (2)	0.0240 (5)
N1	0.7020 (3)	0.77771 (12)	0.53121 (15)	0.0253 (4)
N2	0.3738 (3)	0.69509 (13)	0.59172 (16)	0.0251 (4)
O1	0.7941 (3)	0.95074 (11)	0.75885 (15)	0.0331 (4)
O2	0.8349 (2)	0.80701 (10)	0.79532 (13)	0.0256 (3)
O1W	1.4570 (4)	0.98510 (18)	1.59374 (17)	0.0537 (6)
O3	1.4401 (2)	0.77476 (12)	0.84210 (14)	0.0323 (4)
O4	1.2381 (2)	0.86940 (12)	0.73066 (14)	0.0323 (4)
O5	1.3290 (3)	0.95633 (14)	1.36461 (15)	0.0406 (4)
H5	1.4105	0.9685	1.4244	0.061*
O6	1.5975 (3)	0.97879 (13)	1.25429 (17)	0.0402 (4)
O7	1.2819 (3)	1.12253 (12)	1.23587 (16)	0.0358 (4)
O8	1.0345 (3)	1.16299 (13)	1.09436 (17)	0.0443 (5)
H8	1.0703	1.2125	1.1181	0.066*
Cu1	0.59195 (3)	0.760541 (17)	0.697564 (19)	0.02264 (7)
HW11	1.378 (5)	0.952 (2)	1.625 (3)	0.050 (10)*
HW12	1.575 (4)	0.969 (3)	1.613 (4)	0.078 (14)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0300 (12)	0.0339 (14)	0.0336 (12)	-0.0050 (11)	0.0001 (10)	0.0004 (10)
C2	0.0364 (14)	0.0379 (15)	0.0413 (13)	-0.0056 (12)	0.0101 (11)	0.0070 (11)
C3	0.0433 (15)	0.0387 (14)	0.0276 (11)	0.0050 (11)	0.0095 (10)	0.0068 (9)
C4	0.0351 (11)	0.0263 (13)	0.0238 (9)	0.0057 (11)	0.0014 (8)	0.0009 (9)
C5	0.0486 (16)	0.0344 (15)	0.0218 (10)	0.0106 (11)	-0.0018 (10)	-0.0044 (9)
C6	0.0425 (15)	0.0343 (14)	0.0292 (11)	0.0029 (12)	-0.0098 (10)	-0.0086 (10)
C7	0.0311 (12)	0.0253 (12)	0.0300 (11)	0.0023 (10)	-0.0023 (9)	-0.0075 (9)
C8	0.0286 (12)	0.0344 (14)	0.0446 (14)	-0.0020 (11)	-0.0059 (10)	-0.0113 (10)
C9	0.0314 (13)	0.0350 (15)	0.0465 (14)	-0.0084 (11)	0.0030 (11)	-0.0058 (11)
C10	0.0318 (13)	0.0335 (14)	0.0339 (12)	-0.0055 (11)	0.0066 (10)	-0.0044 (10)
C11	0.0260 (11)	0.0210 (11)	0.0244 (10)	0.0044 (9)	-0.0014 (8)	-0.0037 (8)
C12	0.0270 (10)	0.0196 (13)	0.0240 (9)	0.0042 (8)	-0.0003 (8)	-0.0017 (7)
C13	0.0199 (10)	0.0184 (11)	0.0194 (9)	-0.0018 (8)	0.0014 (8)	-0.0009 (7)
C14	0.0236 (11)	0.0192 (10)	0.0229 (10)	0.0006 (9)	-0.0049 (8)	-0.0024 (8)
C15	0.0198 (10)	0.0224 (11)	0.0236 (10)	-0.0003 (8)	-0.0002 (8)	-0.0015 (8)
C16	0.0233 (10)	0.0187 (10)	0.0208 (9)	-0.0020 (8)	-0.0007 (8)	-0.0015 (7)
C17	0.0175 (10)	0.0259 (12)	0.0247 (10)	0.0002 (9)	-0.0007 (8)	-0.0037 (8)
C18	0.0199 (10)	0.0215 (11)	0.0190 (9)	0.0006 (8)	-0.0004 (7)	-0.0012 (7)
C19	0.0284 (12)	0.0312 (13)	0.0276 (11)	-0.0119 (10)	0.0062 (9)	-0.0042 (9)
C20	0.0357 (12)	0.0215 (11)	0.0223 (10)	-0.0076 (10)	-0.0026 (9)	0.0017 (8)
C21	0.0182 (10)	0.0220 (12)	0.0216 (10)	-0.0008 (9)	-0.0006 (8)	-0.0013 (8)

C22	0.0212 (10)	0.0254 (12)	0.0248 (10)	-0.0034 (8)	0.0036 (8)	-0.0029 (8)
C23	0.0330 (13)	0.0197 (11)	0.0256 (10)	0.0030 (9)	-0.0043 (9)	0.0010 (8)
C24	0.0238 (11)	0.0221 (12)	0.0262 (11)	0.0028 (9)	0.0031 (9)	-0.0032 (8)
N1	0.0252 (9)	0.0254 (12)	0.0251 (8)	-0.0010 (8)	0.0008 (7)	-0.0022 (7)
N2	0.0242 (9)	0.0245 (10)	0.0264 (9)	0.0010 (8)	0.0006 (7)	-0.0030 (7)
O1	0.0381 (10)	0.0263 (9)	0.0323 (9)	0.0023 (8)	-0.0117 (7)	0.0020 (7)
O2	0.0265 (8)	0.0205 (8)	0.0283 (7)	-0.0040 (7)	-0.0051 (6)	-0.0019 (6)
O1W	0.0514 (14)	0.0778 (17)	0.0291 (9)	-0.0253 (13)	-0.0121 (9)	0.0156 (10)
O3	0.0290 (8)	0.0397 (12)	0.0282 (7)	0.0106 (8)	0.0033 (6)	-0.0084 (7)
O4	0.0349 (9)	0.0392 (10)	0.0225 (7)	0.0009 (8)	0.0016 (6)	0.0024 (7)
O5	0.0447 (10)	0.0543 (13)	0.0211 (7)	-0.0153 (9)	-0.0054 (7)	-0.0004 (7)
O6	0.0254 (9)	0.0509 (13)	0.0424 (10)	0.0001 (8)	-0.0069 (7)	-0.0105 (8)
O7	0.0387 (10)	0.0224 (9)	0.0427 (10)	0.0004 (7)	-0.0164 (8)	-0.0049 (7)
O8	0.0502 (11)	0.0249 (10)	0.0528 (11)	0.0103 (9)	-0.0222 (9)	-0.0094 (8)
Cu1	0.02218 (12)	0.02490 (13)	0.02043 (10)	-0.00053 (12)	-0.00032 (8)	-0.00387 (11)

Geometric parameters (Å, °)

C1—N1	1.326 (3)	C15—C16	1.548 (3)
C1—C2	1.398 (3)	C15—H15	0.98
C1—H1	0.93	C16—C23	1.515 (3)
C2—C3	1.364 (4)	C16—C17	1.552 (3)
C2—H2	0.93	C16—H16	0.98
C3—C4	1.405 (4)	C17—C19	1.511 (3)
C3—H3	0.93	C17—C18	1.564 (3)
C4—C12	1.401 (3)	C17—H17	0.98
C4—C5	1.448 (3)	C18—C22	1.523 (3)
C5—C6	1.346 (4)	C18—H18	0.98
C5—H5A	0.93	C19—C20	1.318 (3)
C6—C7	1.440 (3)	C19—H19	0.93
C6—H6	0.93	C20—H20	0.93
C7—C11	1.401 (3)	C21—O1	1.220 (3)
C7—C8	1.410 (3)	C21—O2	1.298 (3)
C8—C9	1.367 (3)	C22—O4	1.236 (3)
C8—H8B	0.93	C22—O3	1.279 (3)
C9—C10	1.399 (3)	C23—O6	1.198 (3)
C9—H9	0.93	C23—O5	1.334 (3)
C10—N2	1.323 (3)	C24—O7	1.200 (3)
C10—H10	0.93	C24—O8	1.320 (3)
C11—N2	1.354 (3)	N1—Cu1	2.0072 (17)
C11—C12	1.434 (3)	N2—Cu1	2.0119 (19)
C12—N1	1.356 (3)	O2—Cu1	1.9640 (15)
C13—C21	1.525 (3)	O1W—HW11	0.82 (3)
C13—C14	1.540 (3)	O1W—HW12	0.822 (19)
C13—C18	1.556 (3)	O3—Cu1 ⁱ	1.9355 (15)
C13—H13	0.98	O5—H5	0.82
C14—C20	1.505 (3)	O7—Cu1 ⁱⁱ	2.3398 (18)
C14—C15	1.554 (3)	O8—H8	0.82

supplementary materials

C14—H14	0.98	Cu1—O3 ⁱⁱⁱ	1.9355 (15)
C15—C24	1.516 (3)	Cu1—O7 ^{iv}	2.3398 (18)
N1—C1—C2	122.0 (2)	C15—C16—C17	108.75 (16)
N1—C1—H1	119.0	C23—C16—H16	105.8
C2—C1—H1	119.0	C15—C16—H16	105.8
C3—C2—C1	119.7 (2)	C17—C16—H16	105.8
C3—C2—H2	120.2	C19—C17—C16	111.41 (18)
C1—C2—H2	120.2	C19—C17—C18	106.48 (17)
C2—C3—C4	120.0 (2)	C16—C17—C18	105.53 (16)
C2—C3—H3	120.0	C19—C17—H17	111.1
C4—C3—H3	120.0	C16—C17—H17	111.1
C12—C4—C3	116.4 (2)	C18—C17—H17	111.1
C12—C4—C5	118.2 (2)	C22—C18—C13	116.14 (16)
C3—C4—C5	125.3 (2)	C22—C18—C17	108.15 (17)
C6—C5—C4	121.3 (2)	C13—C18—C17	106.20 (16)
C6—C5—H5A	119.4	C22—C18—H18	108.7
C4—C5—H5A	119.4	C13—C18—H18	108.7
C5—C6—C7	121.6 (2)	C17—C18—H18	108.7
C5—C6—H6	119.2	C20—C19—C17	114.4 (2)
C7—C6—H6	119.2	C20—C19—H19	122.8
C11—C7—C8	116.8 (2)	C17—C19—H19	122.8
C11—C7—C6	118.0 (2)	C19—C20—C14	113.8 (2)
C8—C7—C6	125.2 (2)	C19—C20—H20	123.1
C9—C8—C7	119.4 (2)	C14—C20—H20	123.1
C9—C8—H8B	120.3	O1—C21—O2	124.26 (19)
C7—C8—H8B	120.3	O1—C21—C13	121.4 (2)
C8—C9—C10	119.8 (2)	O2—C21—C13	114.15 (18)
C8—C9—H9	120.1	O4—C22—O3	124.92 (19)
C10—C9—H9	120.1	O4—C22—C18	121.8 (2)
N2—C10—C9	122.1 (2)	O3—C22—C18	113.28 (18)
N2—C10—H10	119.0	O6—C23—O5	124.8 (2)
C9—C10—H10	119.0	O6—C23—C16	125.9 (2)
N2—C11—C7	123.2 (2)	O5—C23—C16	109.01 (19)
N2—C11—C12	116.08 (19)	O7—C24—O8	122.7 (2)
C7—C11—C12	120.70 (19)	O7—C24—C15	123.8 (2)
N1—C12—C4	123.4 (2)	O8—C24—C15	113.40 (19)
N1—C12—C11	116.42 (17)	C1—N1—C12	118.41 (18)
C4—C12—C11	120.14 (19)	C1—N1—Cu1	128.81 (15)
C21—C13—C14	114.04 (17)	C12—N1—Cu1	112.72 (14)
C21—C13—C18	115.24 (16)	C10—N2—C11	118.6 (2)
C14—C13—C18	110.05 (17)	C10—N2—Cu1	128.54 (16)
C21—C13—H13	105.5	C11—N2—Cu1	112.83 (15)
C14—C13—H13	105.5	C21—O2—Cu1	125.43 (14)
C18—C13—H13	105.5	HW11—O1W—HW12	109 (4)
C20—C14—C13	111.19 (17)	C22—O3—Cu1 ⁱ	114.82 (14)
C20—C14—C15	105.24 (17)	C23—O5—H5	109.5
C13—C14—C15	107.38 (17)	C24—O7—Cu1 ⁱⁱ	130.37 (16)
C20—C14—H14	110.9	C24—O8—H8	109.5

C13—C14—H14	110.9	O3 ⁱⁱⁱ —Cu1—O2	89.24 (7)
C15—C14—H14	110.9	O3 ⁱⁱⁱ —Cu1—N1	162.98 (7)
C24—C15—C16	114.85 (17)	O2—Cu1—N1	94.97 (7)
C24—C15—C14	110.54 (18)	O3 ⁱⁱⁱ —Cu1—N2	96.53 (7)
C16—C15—C14	107.01 (16)	O2—Cu1—N2	170.11 (7)
C24—C15—H15	108.1	N1—Cu1—N2	81.84 (7)
C16—C15—H15	108.1	O3 ⁱⁱⁱ —Cu1—O7 ^{iv}	92.84 (7)
C14—C15—H15	108.1	O2—Cu1—O7 ^{iv}	84.71 (6)
C23—C16—C15	116.02 (18)	N1—Cu1—O7 ^{iv}	103.96 (7)
C23—C16—C17	113.89 (18)	N2—Cu1—O7 ^{iv}	86.97 (7)
N1—C1—C2—C3	0.4 (4)	C15—C14—C20—C19	57.3 (2)
C1—C2—C3—C4	0.2 (4)	C14—C13—C21—O1	-1.8 (3)
C2—C3—C4—C12	-0.3 (4)	C18—C13—C21—O1	-130.5 (2)
C2—C3—C4—C5	178.6 (2)	C14—C13—C21—O2	-177.45 (17)
C12—C4—C5—C6	-2.2 (4)	C18—C13—C21—O2	53.9 (2)
C3—C4—C5—C6	178.8 (3)	C13—C18—C22—O4	17.8 (3)
C4—C5—C6—C7	0.4 (4)	C17—C18—C22—O4	-101.4 (2)
C5—C6—C7—C11	2.0 (4)	C13—C18—C22—O3	-164.32 (18)
C5—C6—C7—C8	-176.8 (3)	C17—C18—C22—O3	76.5 (2)
C11—C7—C8—C9	0.9 (4)	C15—C16—C23—O6	-114.2 (3)
C6—C7—C8—C9	179.8 (2)	C17—C16—C23—O6	13.2 (3)
C7—C8—C9—C10	0.3 (4)	C15—C16—C23—O5	71.4 (2)
C8—C9—C10—N2	-0.4 (4)	C17—C16—C23—O5	-161.24 (19)
C8—C7—C11—N2	-2.3 (3)	C16—C15—C24—O7	-23.1 (3)
C6—C7—C11—N2	178.8 (2)	C14—C15—C24—O7	-144.3 (2)
C8—C7—C11—C12	176.3 (2)	C16—C15—C24—O8	160.03 (19)
C6—C7—C11—C12	-2.6 (3)	C14—C15—C24—O8	38.8 (2)
C3—C4—C12—N1	-0.1 (3)	C2—C1—N1—C12	-0.8 (4)
C5—C4—C12—N1	-179.1 (2)	C2—C1—N1—Cu1	-177.84 (18)
C3—C4—C12—C11	-179.3 (2)	C4—C12—N1—C1	0.6 (3)
C5—C4—C12—C11	1.6 (3)	C11—C12—N1—C1	179.9 (2)
N2—C11—C12—N1	0.2 (3)	C4—C12—N1—Cu1	178.13 (18)
C7—C11—C12—N1	-178.5 (2)	C11—C12—N1—Cu1	-2.6 (2)
N2—C11—C12—C4	179.5 (2)	C9—C10—N2—C11	-0.9 (4)
C7—C11—C12—C4	0.8 (3)	C9—C10—N2—Cu1	-179.39 (19)
C21—C13—C14—C20	-88.1 (2)	C7—C11—N2—C10	2.3 (3)
C18—C13—C14—C20	43.2 (2)	C12—C11—N2—C10	-176.4 (2)
C21—C13—C14—C15	157.29 (17)	C7—C11—N2—Cu1	-179.00 (18)
C18—C13—C14—C15	-71.42 (19)	C12—C11—N2—Cu1	2.3 (2)
C20—C14—C15—C24	56.4 (2)	O1—C21—O2—Cu1	-23.2 (3)
C13—C14—C15—C24	174.93 (17)	C13—C21—O2—Cu1	152.23 (14)
C20—C14—C15—C16	-69.3 (2)	O4—C22—O3—Cu1 ⁱ	9.8 (3)
C13—C14—C15—C16	49.2 (2)	C18—C22—O3—Cu1 ⁱ	-167.97 (14)
C24—C15—C16—C23	26.6 (3)	O8—C24—O7—Cu1 ⁱⁱ	-7.8 (4)
C14—C15—C16—C23	149.70 (18)	C15—C24—O7—Cu1 ⁱⁱ	175.59 (14)
C24—C15—C16—C17	-103.3 (2)	C21—O2—Cu1—O3 ⁱⁱⁱ	-77.88 (17)

supplementary materials

C14—C15—C16—C17	19.8 (2)	C21—O2—Cu1—N1	85.60 (17)
C23—C16—C17—C19	-91.2 (2)	C21—O2—Cu1—O7 ^{iv}	-170.81 (17)
C15—C16—C17—C19	39.8 (2)	C1—N1—Cu1—O3 ⁱⁱⁱ	94.5 (3)
C23—C16—C17—C18	153.60 (18)	C12—N1—Cu1—O3 ⁱⁱⁱ	-82.7 (3)
C15—C16—C17—C18	-75.3 (2)	C1—N1—Cu1—O2	-9.3 (2)
C21—C13—C18—C22	26.2 (3)	C12—N1—Cu1—O2	173.52 (15)
C14—C13—C18—C22	-104.5 (2)	C1—N1—Cu1—N2	-179.9 (2)
C21—C13—C18—C17	146.43 (17)	C12—N1—Cu1—N2	2.94 (15)
C14—C13—C18—C17	15.8 (2)	C1—N1—Cu1—O7 ^{iv}	-95.1 (2)
C19—C17—C18—C22	59.7 (2)	C12—N1—Cu1—O7 ^{iv}	87.74 (15)
C16—C17—C18—C22	178.16 (17)	C10—N2—Cu1—O3 ⁱⁱⁱ	-21.4 (2)
C19—C17—C18—C13	-65.7 (2)	C11—N2—Cu1—O3 ⁱⁱⁱ	160.06 (15)
C16—C17—C18—C13	52.9 (2)	C10—N2—Cu1—N1	175.7 (2)
C16—C17—C19—C20	-57.8 (2)	C11—N2—Cu1—N1	-2.86 (15)
C18—C17—C19—C20	56.8 (2)	C10—N2—Cu1—O7 ^{iv}	71.1 (2)
C17—C19—C20—C14	5.7 (3)	C11—N2—Cu1—O7 ^{iv}	-107.43 (15)
C13—C14—C20—C19	-58.6 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O1W	0.82	1.84	2.567 (2)	148
O8—H8 \cdots O2 ⁱⁱ	0.82	1.79	2.594 (2)	166
O1W—HW11 \cdots O4 ^v	0.82 (3)	1.97 (3)	2.777 (3)	167 (3)
O1W—HW12 \cdots O1 ^{vi}	0.82 (2)	2.05 (3)	2.763 (3)	145 (4)

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

Fig. 2

