Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# *catena*-Poly[[[aqua(pyrazino[2,3-*f*][1,10]phenanthroline)copper(II)]-$\mu$-benzene-1,3-dicarboxylato] *N*,*N*-dimethylacetamide monohydrate]

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Received 10 May 2007; accepted 10 May 2007

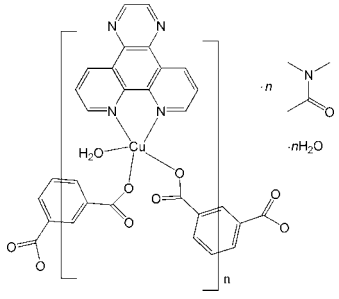
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.007 Å; $R$ factor = 0.068; $wR$ factor = 0.184; data-to-parameter ratio = 15.6.

In the title compound, $[Cu(C_8H_4O_4)(C_{14}H_8N_4)(H_2O)]\cdot C_4H_9NO\cdot H_2O$, the $Cu^{II}$ atom is five-coordinated by three O atoms from two benzene-1,3-dicarboxylate (1,3-bdc) ligands and one water molecule, and two N atoms from one chelating pyrazino[2,3-*f*][1,10]phenanthroline (*L*) ligand in a distorted square-pyramidal geometry. The $Cu^{II}$ atoms are bridged by the 1,3-bdc ligands to form a one-dimensional helical chain structure. A network of O—H···O hydrogen bonds completes the structure. There are two half-molecules of 1,3-bdc in the asymmetric unit; both complete molecules are generated by twofold rotation symmetry, with two C atoms lying on the rotation axis in each case.

## Related literature

One related helical coordination polymer, $[Cu(1,4\text{-bdc})(L)(H_2O)]$, where 1,4-bdc is the benzene-1,4-dicarboxylate dianion, has been reported. In this compound, the $Cu^{II}$ atom is five-coordinate and exhibits a distorted square-pyramidal coordination environment. The $Cu^{II}$ atoms are bridged by the 1,4-bdc ligands to form a one-dimensional helical chain structure (Zhang *et al.*, 2007).

For related literature, see: Cai *et al.* (2006); Dickeson & Summers (1970); Ren & Zhao (2006); Yang *et al.* (2005).




## Experimental

### *Crystal data*

$[Cu(C_8H_4O_4)(C_{14}H_8N_4)(H_2O)]\cdot C_4H_9NO\cdot H_2O$
$M_r$ = 583.05
Monoclinic, $P2/c$
$a$ = 14.829 (3) Å
$b$ = 7.2111 (14) Å
$c$ = 23.976 (5) Å
$\beta$ = 95.00 (3)°
$V$ = 2554.1 (9) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.91 mm$^{-1}$
$T$ = 293 (2) K
0.33 × 0.31 × 0.30 mm

### *Data collection*

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.733, $T_{max}$ = 0.766
23862 measured reflections
5813 independent reflections
4102 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.061

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.184
$S$ = 1.07
5813 reflections
373 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.09 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.43 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.026 (4) | Cu1—O3 | 1.947 (3) |
| Cu1—N2 | 2.043 (4) | Cu1—O1*W* | 2.324 (4) |
| Cu1—O2 | 1.920 (3) | | |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H*W*12···O2*W*$^{i}$ | 0.86 (4) | 1.93 (2) | 2.765 (6) | 162 (5) |
| O1*W*—H*W*11···O5 | 0.85 (4) | 1.94 (2) | 2.772 (5) | 165 (5) |
| O2*W*—H*W*22···O1 | 0.86 (6) | 2.10 (4) | 2.740 (6) | 131 (4) |
| O2*W*—H*W*21···O4 | 0.85 (4) | 1.92 (4) | 2.732 (6) | 159 (9) |

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

The work was supported by Program for Young Academic Backbone in Heilongjiang Provincial University (No. 1152G053).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2408).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m1692-m1693 [ **doi:10.1107/S1600536807023082** ]

# *catena*-Poly[[[aqua(pyrazino[2,3-*f*][1,10]phenanthroline)copper(II)]-$\mu$-benzene-1,3-dicarboxylato] *N*,*N*-dimethylacetamide monohydrate]

**W.-Z. Zhang**

## Comment

Recently, helical structures have received intense interest in coordination chemistry (Cai *et al.*, 2006). It is well known that a bidentate organic acid ligand may be useful in the formation of helical chains in the presence of 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen). The N atoms from the bipy or phen ligand may occupy two coordination positions of central metals (Ren & Zhao, 2006). The additional coordination positions are available for the bidentate carboxylate ligands, leading to the formation of a helix (Yang *et al.*, 2005).

We therefore selected benzene-1,3-dicarboxylic acid (1,3-bdc$H_2$) as a bridging ligand and pyrazino[2,3-*f*][1,10]phenanthroline (*L*) as a secondary ligand, forming a the title compound, (I), a new helical Cu(II) coordination polymer, [Cu(1,3-bdc)(*L*)($H_2O$)]·DMA·$H_2O$ (DMA = *N*,*N*-dimethylacetamide), which is reported here.

Selected bond lengths and angles for (I) are given in Table 1. In (I) each $Cu^{II}$ atom is five-coordinated by three O atoms from two monodentate 1,3-bdc ligands and one water molecule, and two N atoms from one chelating *L* ligand in a distorted square-pyramidal coordination sphere (Fig. 1). Two carboxylate O atoms (O2, O3) and two N atoms (N1, N2) form the equatorial plane, whereas the water molecule occupies the axial position with Cu1—O1w distance of 2.324 (4) Å.

The 1,3-bdc ligands linked the $Cu^{II}$ atoms to form a one-dimensional helical chain structure (Fig. 2). The helical chain is decorated with *L* ligands, alternately at each side. Finally, O—H···O H-bonds complete the structure of (I) (Table 2).

## Experimental

The *L* ligand was synthesized according to the literature method (Dickeson & Summers, 1970). A *N*,*N*-dimethylacetamide solution (15 ml) of *L* (121 mg, 0.5 mmol) was mixed with an aqueous solution (6 ml) of $ClCl_2·2H_2O$ (86 mg, 0.5 mmol) with stirring at 385 K. Then the 1,3-bdc$H_2$ was added to the mixture with stirring. The resulting solution was filtered, the filtrate was allowed to stand in air at room temperature for two weeks, and blue crystals of (I) were obtained (yield 29% based on Cu).

## Refinement

All H atoms on C atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}$(H)=1.2$U_{eq}$(carrier). The water H-atoms were located in a difference Fourier map, and were refined with distance restraints of O–H = 0.85 (1) Å; $U_{iso}$ was allowed to refine freely.

**Figures**

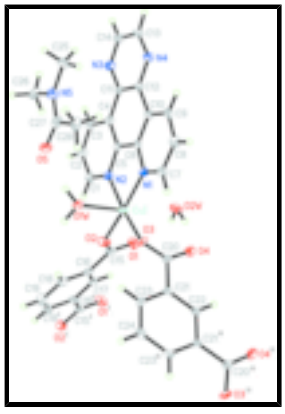

Fig. 1. The structure of (I), with displacement ellipsoids drawn at the 30% probability level (arbitrary spheres for the H atoms). Symmetry codes: (i) 1 − *x*, *y*, 3/2 − *z*; (ii) −*x*, *y*, 3/2 − *z*.

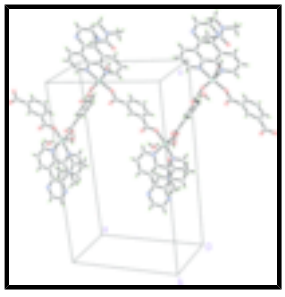

Fig. 2. View of part of the helical chain structure of (I) with DMA and uncoordinated water molecules omitted for clarity.

**_catena_-Poly[[[aqua(pyrazino[2,3-_f_][1,10]phenanthroline)copper(II)]-μ- benzene-1,3-dicarboxylato] _N_,_N_-dimethylacetamide monohydrate]**

*Crystal data*

| | |
|---|---|
| $[Cu(C_8H_4O_4)(C_{14}H_8N_4)(H_2O)]\cdot C_4H_9NO\cdot H_2O$ | $F_{000}$ = 1204 |
| $M_r$ = 583.05 | $D_x$ = 1.516 Mg m$^{-3}$ |
| Monoclinic, *P*2/*c* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2yc | Cell parameters from 17473 reflections |
| *a* = 14.829 (3) Å | θ = 3.2–27.5º |
| *b* = 7.2111 (14) Å | μ = 0.91 mm$^{-1}$ |
| *c* = 23.976 (5) Å | *T* = 293 (2) K |
| β = 95.00 (3)º | Block, blue |
| *V* = 2554.1 (9) Å$^3$ | 0.33 × 0.31 × 0.30 mm |
| *Z* = 4 | |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 5813 independent reflections |
| Radiation source: rotating anode | 4102 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.061 |
| Detector resolution: 10.0 pixels mm$^{-1}$ | $\theta_{max}$ = 27.5º |

| | |
|---|---|
| $T$ = 293(2) K | $\theta_{min}$ = 3.1° |
| ω scans | $h$ = −19→18 |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $k$ = −9→9 |
| $T_{min}$ = 0.733, $T_{max}$ = 0.766 | $l$ = −31→31 |
| 23862 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.068 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.184 | $w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 7.6293P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.07 | $(\Delta/\sigma)_{max} < 0.001$ |
| 5813 reflections | $\Delta\rho_{max}$ = 1.09 e Å$^{-3}$ |
| 373 parameters | $\Delta\rho_{min}$ = −0.43 e Å$^{-3}$ |
| 7 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*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 | 0.4129 (3) | 0.2052 (8) | 0.5417 (2) | 0.0440 (12) |
| H1 | 0.4376 | 0.1590 | 0.5759 | 0.053* |
| C2 | 0.4719 (3) | 0.2530 (8) | 0.5017 (2) | 0.0497 (13) |
| H2 | 0.5342 | 0.2429 | 0.5097 | 0.060* |
| C3 | 0.4370 (3) | 0.3140 (7) | 0.4510 (2) | 0.0440 (11) |
| H3 | 0.4752 | 0.3432 | 0.4235 | 0.053* |
| C4 | 0.3426 (3) | 0.3333 (6) | 0.43985 (18) | 0.0357 (10) |
| C5 | 0.2887 (3) | 0.2852 (6) | 0.48253 (17) | 0.0314 (9) |
| C6 | 0.1916 (3) | 0.2943 (6) | 0.47436 (17) | 0.0297 (9) |
| C7 | 0.0563 (3) | 0.2370 (7) | 0.5113 (2) | 0.0424 (11) |

| | | | | |
|---|---|---|---|---|
| H7 | 0.0246 | 0.1983 | 0.5411 | 0.051* |
| C8 | 0.0072 (3) | 0.2930 (8) | 0.4617 (2) | 0.0475 (12) |
| H8 | −0.0558 | 0.2909 | 0.4587 | 0.057* |
| C9 | 0.0525 (3) | 0.3505 (7) | 0.4178 (2) | 0.0422 (11) |
| H9 | 0.0208 | 0.3879 | 0.3845 | 0.051* |
| C10 | 0.1472 (3) | 0.3528 (6) | 0.42319 (18) | 0.0339 (9) |
| C11 | 0.2981 (3) | 0.3891 (6) | 0.38611 (18) | 0.0376 (10) |
| C12 | 0.2044 (3) | 0.4006 (6) | 0.37806 (17) | 0.0346 (10) |
| C13 | 0.2132 (4) | 0.4844 (7) | 0.2878 (2) | 0.0522 (14) |
| H13 | 0.1863 | 0.5186 | 0.2528 | 0.063* |
| C14 | 0.3063 (5) | 0.4713 (8) | 0.2957 (2) | 0.0570 (15) |
| H14 | 0.3395 | 0.4941 | 0.2652 | 0.068* |
| C15 | 0.3677 (3) | 0.1853 (8) | 0.67698 (17) | 0.0414 (12) |
| C16 | 0.4361 (3) | 0.0762 (7) | 0.71521 (17) | 0.0361 (10) |
| C17 | 0.5000 | 0.1725 (9) | 0.7500 | 0.0340 (13) |
| H17 | 0.5000 | 0.3015 | 0.7500 | 0.041* |
| C18 | 0.4360 (3) | −0.1149 (8) | 0.7155 (2) | 0.0456 (12) |
| H18 | 0.3931 | −0.1798 | 0.6925 | 0.055* |
| C19 | 0.5000 | −0.2104 (12) | 0.7500 | 0.058 (2) |
| H19 | 0.5000 | −0.3394 | 0.7500 | 0.070* |
| C20 | 0.0931 (3) | 0.2029 (7) | 0.66650 (17) | 0.0352 (10) |
| C21 | 0.0441 (3) | 0.0973 (6) | 0.70954 (16) | 0.0319 (9) |
| C22 | 0.0000 | 0.1949 (9) | 0.7500 | 0.0318 (13) |
| H22 | 0.0000 | 0.3239 | 0.7500 | 0.038* |
| C23 | 0.0432 (3) | −0.0947 (7) | 0.71019 (19) | 0.0407 (11) |
| H23 | 0.0721 | −0.1597 | 0.6834 | 0.049* |
| C24 | 0.0000 | −0.1916 (10) | 0.7500 | 0.0461 (17) |
| H24 | 0.0000 | −0.3206 | 0.7500 | 0.055* |
| C25 | 0.2265 (4) | −0.0370 (9) | 0.3096 (2) | 0.0595 (16) |
| H25A | 0.2479 | 0.0777 | 0.2953 | 0.089* |
| H25B | 0.1640 | −0.0243 | 0.3165 | 0.089* |
| H25C | 0.2326 | −0.1338 | 0.2827 | 0.089* |
| C26 | 0.3805 (4) | −0.0846 (9) | 0.3637 (2) | 0.0552 (14) |
| H26A | 0.3996 | −0.0077 | 0.3343 | 0.083* |
| H26B | 0.4014 | −0.2091 | 0.3589 | 0.083* |
| H26C | 0.4055 | −0.0376 | 0.3992 | 0.083* |
| C27 | 0.2456 (5) | −0.1394 (8) | 0.4071 (3) | 0.0586 (15) |
| C28 | 0.1422 (3) | −0.1422 (8) | 0.4065 (3) | 0.0530 (13) |
| H28A | 0.1174 | −0.2215 | 0.3768 | 0.080* |
| H28B | 0.1191 | −0.0188 | 0.4005 | 0.080* |
| H28C | 0.1253 | −0.1880 | 0.4417 | 0.080* |
| N1 | 0.1455 (2) | 0.2367 (5) | 0.51787 (14) | 0.0328 (8) |
| N2 | 0.3234 (2) | 0.2223 (6) | 0.53358 (15) | 0.0347 (8) |
| N3 | 0.3510 (3) | 0.4285 (6) | 0.34392 (18) | 0.0497 (11) |
| N4 | 0.1615 (3) | 0.4498 (6) | 0.32826 (16) | 0.0465 (10) |
| N5 | 0.2799 (3) | −0.0837 (7) | 0.36185 (19) | 0.0558 (12) |
| O1 | 0.3691 (3) | 0.3545 (6) | 0.67766 (17) | 0.0612 (11) |
| O2 | 0.3140 (2) | 0.0834 (6) | 0.64574 (14) | 0.0533 (10) |
| O1W | 0.2181 (3) | −0.1484 (5) | 0.55112 (14) | 0.0475 (9) |

| | | | | |
|---|---|---|---|---|
| HW11 | 0.241 (4) | −0.181 (7) | 0.5213 (13) | 0.064 (19)* |
| HW12 | 0.234 (3) | −0.239 (5) | 0.5731 (15) | 0.044 (15)* |
| O3 | 0.1262 (2) | 0.1001 (6) | 0.63021 (13) | 0.0490 (9) |
| O2W | 0.2320 (3) | 0.5306 (7) | 0.61437 (18) | 0.0654 (12) |
| HW21 | 0.186 (3) | 0.510 (12) | 0.632 (3) | 0.11 (3)* |
| HW22 | 0.276 (3) | 0.545 (7) | 0.640 (3) | 0.14 (4)* |
| O4 | 0.0964 (3) | 0.3738 (5) | 0.66852 (15) | 0.0518 (9) |
| O5 | 0.2951 (3) | −0.1872 (6) | 0.45047 (14) | 0.0563 (10) |
| Cu1 | 0.22665 (4) | 0.15296 (9) | 0.58553 (2) | 0.03622 (19) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.035 (2) | 0.057 (3) | 0.039 (2) | 0.001 (2) | −0.004 (2) | 0.000 (2) |
| C2 | 0.031 (2) | 0.066 (4) | 0.052 (3) | −0.003 (2) | 0.003 (2) | −0.001 (3) |
| C3 | 0.042 (3) | 0.046 (3) | 0.046 (3) | −0.007 (2) | 0.016 (2) | 0.001 (2) |
| C4 | 0.038 (2) | 0.035 (2) | 0.034 (2) | −0.005 (2) | 0.0055 (18) | −0.0019 (19) |
| C5 | 0.033 (2) | 0.033 (2) | 0.029 (2) | −0.0013 (18) | 0.0036 (17) | −0.0034 (17) |
| C6 | 0.035 (2) | 0.026 (2) | 0.0284 (19) | 0.0021 (17) | 0.0013 (17) | −0.0028 (16) |
| C7 | 0.034 (2) | 0.054 (3) | 0.040 (2) | 0.000 (2) | 0.006 (2) | 0.005 (2) |
| C8 | 0.027 (2) | 0.062 (3) | 0.053 (3) | 0.003 (2) | 0.000 (2) | 0.002 (3) |
| C9 | 0.041 (2) | 0.044 (3) | 0.039 (2) | 0.007 (2) | −0.006 (2) | −0.001 (2) |
| C10 | 0.041 (2) | 0.030 (2) | 0.031 (2) | 0.0021 (19) | −0.0005 (18) | −0.0013 (18) |
| C11 | 0.050 (3) | 0.032 (2) | 0.031 (2) | −0.002 (2) | 0.010 (2) | 0.0023 (18) |
| C12 | 0.047 (3) | 0.029 (2) | 0.028 (2) | 0.0007 (19) | 0.0039 (18) | 0.0008 (17) |
| C13 | 0.082 (4) | 0.044 (3) | 0.029 (2) | 0.007 (3) | 0.002 (2) | 0.010 (2) |
| C14 | 0.090 (5) | 0.045 (3) | 0.039 (3) | 0.005 (3) | 0.023 (3) | 0.009 (2) |
| C15 | 0.038 (2) | 0.065 (4) | 0.0213 (19) | 0.000 (2) | 0.0000 (18) | 0.001 (2) |
| C16 | 0.032 (2) | 0.050 (3) | 0.026 (2) | −0.002 (2) | 0.0028 (17) | −0.0013 (19) |
| C17 | 0.035 (3) | 0.042 (4) | 0.026 (3) | 0.000 | 0.005 (2) | 0.000 |
| C18 | 0.041 (3) | 0.052 (3) | 0.042 (3) | −0.008 (2) | −0.007 (2) | −0.006 (2) |
| C19 | 0.049 (4) | 0.053 (5) | 0.071 (5) | 0.000 | −0.004 (4) | 0.000 |
| C20 | 0.031 (2) | 0.050 (3) | 0.0251 (19) | 0.002 (2) | 0.0021 (17) | −0.0001 (19) |
| C21 | 0.030 (2) | 0.043 (2) | 0.0222 (18) | −0.0035 (18) | 0.0014 (16) | −0.0005 (17) |
| C22 | 0.033 (3) | 0.040 (3) | 0.023 (3) | 0.000 | 0.002 (2) | 0.000 |
| C23 | 0.047 (3) | 0.044 (3) | 0.032 (2) | 0.005 (2) | 0.008 (2) | −0.008 (2) |
| C24 | 0.062 (5) | 0.030 (4) | 0.047 (4) | 0.000 | 0.007 (3) | 0.000 |
| C25 | 0.080 (4) | 0.052 (3) | 0.044 (3) | 0.000 (3) | −0.014 (3) | 0.010 (3) |
| C26 | 0.044 (3) | 0.069 (4) | 0.055 (3) | −0.003 (3) | 0.017 (2) | −0.012 (3) |
| C27 | 0.073 (4) | 0.045 (3) | 0.061 (3) | −0.003 (3) | 0.017 (3) | −0.014 (3) |
| C28 | 0.037 (3) | 0.055 (3) | 0.068 (3) | 0.001 (2) | 0.010 (2) | −0.009 (3) |
| N1 | 0.0294 (18) | 0.040 (2) | 0.0293 (17) | 0.0012 (16) | 0.0047 (14) | −0.0005 (15) |
| N2 | 0.0292 (18) | 0.045 (2) | 0.0298 (17) | −0.0003 (16) | 0.0007 (14) | −0.0038 (16) |
| N3 | 0.059 (3) | 0.050 (3) | 0.042 (2) | 0.002 (2) | 0.016 (2) | 0.008 (2) |
| N4 | 0.060 (3) | 0.046 (2) | 0.033 (2) | 0.007 (2) | 0.0010 (19) | 0.0024 (18) |
| N5 | 0.060 (3) | 0.062 (3) | 0.046 (2) | 0.000 (2) | 0.004 (2) | 0.000 (2) |
| O1 | 0.065 (3) | 0.056 (3) | 0.059 (2) | 0.015 (2) | −0.018 (2) | −0.006 (2) |
| O2 | 0.052 (2) | 0.068 (3) | 0.0364 (17) | −0.0087 (19) | −0.0164 (16) | 0.0066 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O1W | 0.060 (2) | 0.050 (2) | 0.0331 (17) | 0.0020 (18) | 0.0091 (16) | 0.0023 (16) |
| O3 | 0.050 (2) | 0.069 (2) | 0.0303 (16) | −0.0023 (18) | 0.0203 (15) | −0.0047 (16) |
| O2W | 0.061 (3) | 0.076 (3) | 0.060 (2) | −0.001 (2) | 0.008 (2) | 0.033 (2) |
| O4 | 0.059 (2) | 0.047 (2) | 0.052 (2) | −0.0009 (18) | 0.0232 (18) | 0.0075 (17) |
| O5 | 0.060 (2) | 0.075 (3) | 0.0345 (17) | 0.006 (2) | 0.0035 (16) | 0.0069 (18) |
| Cu1 | 0.0312 (3) | 0.0564 (4) | 0.0209 (2) | 0.0002 (3) | 0.00140 (19) | −0.0004 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—N2 | 1.331 (6) | C18—H18 | 0.9300 |
| C1—C2 | 1.397 (7) | C19—C18$^{i}$ | 1.387 (7) |
| C1—H1 | 0.9300 | C19—H19 | 0.9300 |
| C2—C3 | 1.351 (7) | C20—O4 | 1.234 (6) |
| C2—H2 | 0.9300 | C20—O3 | 1.274 (6) |
| C3—C4 | 1.408 (7) | C20—C21 | 1.518 (6) |
| C3—H3 | 0.9300 | C21—C23 | 1.385 (7) |
| C4—C5 | 1.396 (6) | C21—C22 | 1.405 (5) |
| C4—C11 | 1.453 (6) | C22—C21$^{ii}$ | 1.405 (5) |
| C5—N2 | 1.363 (5) | C22—H22 | 0.9300 |
| C5—C6 | 1.437 (6) | C23—C24 | 1.384 (6) |
| C6—N1 | 1.361 (5) | C23—H23 | 0.9300 |
| C6—C10 | 1.406 (6) | C24—C23$^{ii}$ | 1.384 (6) |
| C7—N1 | 1.318 (6) | C24—H24 | 0.9300 |
| C7—C8 | 1.400 (7) | C25—N5 | 1.462 (7) |
| C7—H7 | 0.9300 | C25—H25A | 0.9600 |
| C8—C9 | 1.362 (7) | C25—H25B | 0.9600 |
| C8—H8 | 0.9300 | C25—H25C | 0.9600 |
| C9—C10 | 1.399 (7) | C26—N5 | 1.489 (7) |
| C9—H9 | 0.9300 | C26—H26A | 0.9600 |
| C10—C12 | 1.473 (6) | C26—H26B | 0.9600 |
| C11—N3 | 1.363 (6) | C26—H26C | 0.9600 |
| C11—C12 | 1.388 (7) | C27—O5 | 1.267 (7) |
| C12—N4 | 1.351 (6) | C27—N5 | 1.302 (7) |
| C13—N4 | 1.311 (7) | C27—C28 | 1.531 (8) |
| C13—C14 | 1.381 (9) | C28—H28A | 0.9600 |
| C13—H13 | 0.9300 | C28—H28B | 0.9600 |
| C14—N3 | 1.318 (7) | C28—H28C | 0.9600 |
| C14—H14 | 0.9300 | Cu1—N1 | 2.026 (4) |
| C15—O1 | 1.221 (7) | Cu1—N2 | 2.043 (4) |
| C15—O2 | 1.277 (6) | Cu1—O2 | 1.920 (3) |
| C15—C16 | 1.525 (7) | Cu1—O3 | 1.947 (3) |
| C16—C18 | 1.378 (7) | Cu1—O1W | 2.324 (4) |
| C16—C17 | 1.392 (6) | O1W—HW11 | 0.85 (4) |
| C17—C16$^{i}$ | 1.392 (6) | O1W—HW12 | 0.86 (4) |
| C17—H17 | 0.9300 | O2W—HW21 | 0.85 (5) |
| C18—C19 | 1.387 (7) | O2W—HW22 | 0.86 (6) |
| N2—C1—C2 | 123.5 (5) | C23—C21—C22 | 119.2 (4) |
| N2—C1—H1 | 118.3 | C23—C21—C20 | 121.0 (4) |

| | | | |
|---|---|---|---|
| C2—C1—H1 | 118.3 | C22—C21—C20 | 119.8 (4) |
| C3—C2—C1 | 119.0 (5) | C21—C22—C21$^{ii}$ | 119.9 (6) |
| C3—C2—H2 | 120.5 | C21—C22—H22 | 120.1 |
| C1—C2—H2 | 120.5 | C21$^{ii}$—C22—H22 | 120.1 |
| C2—C3—C4 | 119.9 (4) | C24—C23—C21 | 121.2 (5) |
| C2—C3—H3 | 120.0 | C24—C23—H23 | 119.4 |
| C4—C3—H3 | 120.0 | C21—C23—H23 | 119.4 |
| C5—C4—C3 | 117.3 (4) | C23$^{ii}$—C24—C23 | 119.4 (6) |
| C5—C4—C11 | 118.3 (4) | C23$^{ii}$—C24—H24 | 120.3 |
| C3—C4—C11 | 124.3 (4) | C23—C24—H24 | 120.3 |
| N2—C5—C4 | 123.0 (4) | N5—C25—H25A | 109.5 |
| N2—C5—C6 | 115.6 (4) | N5—C25—H25B | 109.5 |
| C4—C5—C6 | 121.3 (4) | H25A—C25—H25B | 109.5 |
| N1—C6—C10 | 122.2 (4) | N5—C25—H25C | 109.5 |
| N1—C6—C5 | 116.5 (4) | H25A—C25—H25C | 109.5 |
| C10—C6—C5 | 121.3 (4) | H25B—C25—H25C | 109.5 |
| N1—C7—C8 | 123.0 (4) | N5—C26—H26A | 109.5 |
| N1—C7—H7 | 118.5 | N5—C26—H26B | 109.5 |
| C8—C7—H7 | 118.5 | H26A—C26—H26B | 109.5 |
| C9—C8—C7 | 119.3 (4) | N5—C26—H26C | 109.5 |
| C9—C8—H8 | 120.3 | H26A—C26—H26C | 109.5 |
| C7—C8—H8 | 120.3 | H26B—C26—H26C | 109.5 |
| C8—C9—C10 | 119.4 (4) | O5—C27—N5 | 121.8 (6) |
| C8—C9—H9 | 120.3 | O5—C27—C28 | 120.8 (5) |
| C10—C9—H9 | 120.3 | N5—C27—C28 | 117.3 (6) |
| C9—C10—C6 | 117.9 (4) | C27—C28—H28A | 109.5 |
| C9—C10—C12 | 124.9 (4) | C27—C28—H28B | 109.5 |
| C6—C10—C12 | 117.1 (4) | H28A—C28—H28B | 109.5 |
| N3—C11—C12 | 121.2 (4) | C27—C28—H28C | 109.5 |
| N3—C11—C4 | 118.0 (4) | H28A—C28—H28C | 109.5 |
| C12—C11—C4 | 120.8 (4) | H28B—C28—H28C | 109.5 |
| N4—C12—C11 | 121.8 (4) | C7—N1—C6 | 118.3 (4) |
| N4—C12—C10 | 117.0 (4) | C7—N1—Cu1 | 128.0 (3) |
| C11—C12—C10 | 121.1 (4) | C6—N1—Cu1 | 113.7 (3) |
| N4—C13—C14 | 121.8 (5) | C1—N2—C5 | 117.2 (4) |
| N4—C13—H13 | 119.1 | C1—N2—Cu1 | 129.2 (3) |
| C14—C13—H13 | 119.1 | C5—N2—Cu1 | 113.5 (3) |
| N3—C14—C13 | 123.8 (5) | C14—N3—C11 | 115.0 (5) |
| N3—C14—H14 | 118.1 | C13—N4—C12 | 116.3 (5) |
| C13—C14—H14 | 118.1 | C27—N5—C25 | 124.3 (6) |
| O1—C15—O2 | 126.3 (5) | C27—N5—C26 | 115.9 (5) |
| O1—C15—C16 | 119.9 (4) | C25—N5—C26 | 119.6 (5) |
| O2—C15—C16 | 113.8 (5) | C15—O2—Cu1 | 129.5 (4) |
| C18—C16—C17 | 119.8 (5) | Cu1—O1W—HW11 | 123 (4) |
| C18—C16—C15 | 121.2 (4) | Cu1—O1W—HW12 | 119 (3) |
| C17—C16—C15 | 119.0 (5) | HW11—O1W—HW12 | 101 (3) |
| C16—C17—C16$^{i}$ | 120.2 (6) | C20—O3—Cu1 | 128.4 (3) |
| C16—C17—H17 | 119.9 | HW21—O2W—HW22 | 105 (3) |

| | | | |
|---|---|---|---|
| C16$^{i}$—C17—H17 | 119.9 | O2—Cu1—O3 | 91.92 (16) |
| C16—C18—C19 | 119.9 (5) | O2—Cu1—N1 | 174.00 (16) |
| C16—C18—H18 | 120.0 | O3—Cu1—N1 | 93.99 (15) |
| C19—C18—H18 | 120.0 | O2—Cu1—N2 | 93.37 (16) |
| C18$^{i}$—C19—C18 | 120.4 (8) | O3—Cu1—N2 | 174.49 (15) |
| C18$^{i}$—C19—H19 | 119.8 | N1—Cu1—N2 | 80.69 (14) |
| C18—C19—H19 | 119.8 | O2—Cu1—O1W | 92.00 (16) |
| O4—C20—O3 | 126.3 (4) | O3—Cu1—O1W | 89.51 (15) |
| O4—C20—C21 | 119.6 (4) | N1—Cu1—O1W | 89.09 (14) |
| O3—C20—C21 | 114.1 (4) | N2—Cu1—O1W | 91.83 (14) |
| N2—C1—C2—C3 | −2.4 (9) | C22—C21—C23—C24 | −0.2 (6) |
| C1—C2—C3—C4 | 1.7 (8) | C20—C21—C23—C24 | 178.8 (3) |
| C2—C3—C4—C5 | −0.7 (7) | C21—C23—C24—C23$^{ii}$ | 0.1 (3) |
| C2—C3—C4—C11 | −177.0 (5) | C8—C7—N1—C6 | 0.3 (7) |
| C3—C4—C5—N2 | 0.2 (7) | C8—C7—N1—Cu1 | −177.9 (4) |
| C11—C4—C5—N2 | 176.7 (4) | C10—C6—N1—C7 | −0.2 (6) |
| C3—C4—C5—C6 | −177.9 (4) | C5—C6—N1—C7 | −177.8 (4) |
| C11—C4—C5—C6 | −1.4 (7) | C10—C6—N1—Cu1 | 178.2 (3) |
| N2—C5—C6—N1 | −1.0 (6) | C5—C6—N1—Cu1 | 0.7 (5) |
| C4—C5—C6—N1 | 177.2 (4) | C2—C1—N2—C5 | 1.9 (8) |
| N2—C5—C6—C10 | −178.6 (4) | C2—C1—N2—Cu1 | 177.8 (4) |
| C4—C5—C6—C10 | −0.3 (7) | C4—C5—N2—C1 | −0.8 (7) |
| N1—C7—C8—C9 | −0.1 (8) | C6—C5—N2—C1 | 177.4 (4) |
| C7—C8—C9—C10 | −0.1 (8) | C4—C5—N2—Cu1 | −177.4 (3) |
| C8—C9—C10—C6 | 0.2 (7) | C6—C5—N2—Cu1 | 0.8 (5) |
| C8—C9—C10—C12 | 176.0 (5) | C13—C14—N3—C11 | 2.7 (8) |
| N1—C6—C10—C9 | 0.0 (7) | C12—C11—N3—C14 | −2.1 (7) |
| C5—C6—C10—C9 | 177.4 (4) | C4—C11—N3—C14 | 177.5 (5) |
| N1—C6—C10—C12 | −176.2 (4) | C14—C13—N4—C12 | −0.1 (8) |
| C5—C6—C10—C12 | 1.2 (6) | C11—C12—N4—C13 | 0.6 (7) |
| C5—C4—C11—N3 | −177.4 (4) | C10—C12—N4—C13 | −177.2 (4) |
| C3—C4—C11—N3 | −1.2 (7) | O5—C27—N5—C25 | 176.3 (5) |
| C5—C4—C11—C12 | 2.2 (7) | C28—C27—N5—C25 | −4.6 (8) |
| C3—C4—C11—C12 | 178.4 (5) | O5—C27—N5—C26 | 1.5 (8) |
| N3—C11—C12—N4 | 0.5 (7) | C28—C27—N5—C26 | −179.4 (5) |
| C4—C11—C12—N4 | −179.1 (4) | O1—C15—O2—Cu1 | 6.5 (8) |
| N3—C11—C12—C10 | 178.2 (4) | C16—C15—O2—Cu1 | −172.2 (3) |
| C4—C11—C12—C10 | −1.3 (7) | O4—C20—O3—Cu1 | 25.4 (7) |
| C9—C10—C12—N4 | 1.6 (7) | C21—C20—O3—Cu1 | −156.0 (3) |
| C6—C10—C12—N4 | 177.5 (4) | C15—O2—Cu1—O3 | −107.8 (4) |
| C9—C10—C12—C11 | −176.2 (5) | C15—O2—Cu1—N2 | 70.6 (4) |
| C6—C10—C12—C11 | −0.4 (6) | C15—O2—Cu1—O1W | 162.6 (4) |
| N4—C13—C14—N3 | −1.8 (9) | C20—O3—Cu1—O2 | 82.1 (4) |
| O1—C15—C16—C18 | 179.8 (5) | C20—O3—Cu1—N1 | −96.8 (4) |
| O2—C15—C16—C18 | −1.4 (6) | C20—O3—Cu1—O1W | 174.1 (4) |
| O1—C15—C16—C17 | −0.7 (6) | C7—N1—Cu1—O3 | −3.4 (4) |
| O2—C15—C16—C17 | 178.0 (4) | C6—N1—Cu1—O3 | 178.4 (3) |
| C18—C16—C17—C16$^{i}$ | 0.3 (3) | C7—N1—Cu1—N2 | 178.1 (4) |

| | | | |
|---|---|---|---|
| C15—C16—C17—C16$^{i}$ | −179.2 (4) | C6—N1—Cu1—N2 | −0.2 (3) |
| C17—C16—C18—C19 | −0.5 (7) | C7—N1—Cu1—O1W | 86.1 (4) |
| C15—C16—C18—C19 | 178.9 (4) | C6—N1—Cu1—O1W | −92.2 (3) |
| C16—C18—C19—C18$^{i}$ | 0.3 (3) | C1—N2—Cu1—O2 | 4.4 (5) |
| O4—C20—C21—C23 | −176.6 (5) | C5—N2—Cu1—O2 | −179.4 (3) |
| O3—C20—C21—C23 | 4.6 (6) | C1—N2—Cu1—N1 | −176.4 (5) |
| O4—C20—C21—C22 | 2.4 (6) | C5—N2—Cu1—N1 | −0.3 (3) |
| O3—C20—C21—C22 | −176.4 (3) | C1—N2—Cu1—O1W | −87.7 (4) |
| C23—C21—C22—C21$^{ii}$ | 0.1 (3) | C5—N2—Cu1—O1W | 88.4 (3) |
| C20—C21—C22—C21$^{ii}$ | −178.9 (4) | | |

Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2; (ii) −*x*, *y*, −*z*+3/2.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1W—HW12···O2W$^{iii}$ | 0.86 (4) | 1.93 (2) | 2.765 (6) | 162 (5) |
| O1W—HW11···O5 | 0.85 (4) | 1.94 (2) | 2.772 (5) | 165 (5) |
| O2W—HW22···O1 | 0.86 (6) | 2.10 (4) | 2.740 (6) | 131 (4) |
| O2W—HW21···O4 | 0.85 (4) | 1.92 (4) | 2.732 (6) | 159 (9) |

Symmetry codes: (iii) *x*, *y*−1, *z*.

**Fig. 1**

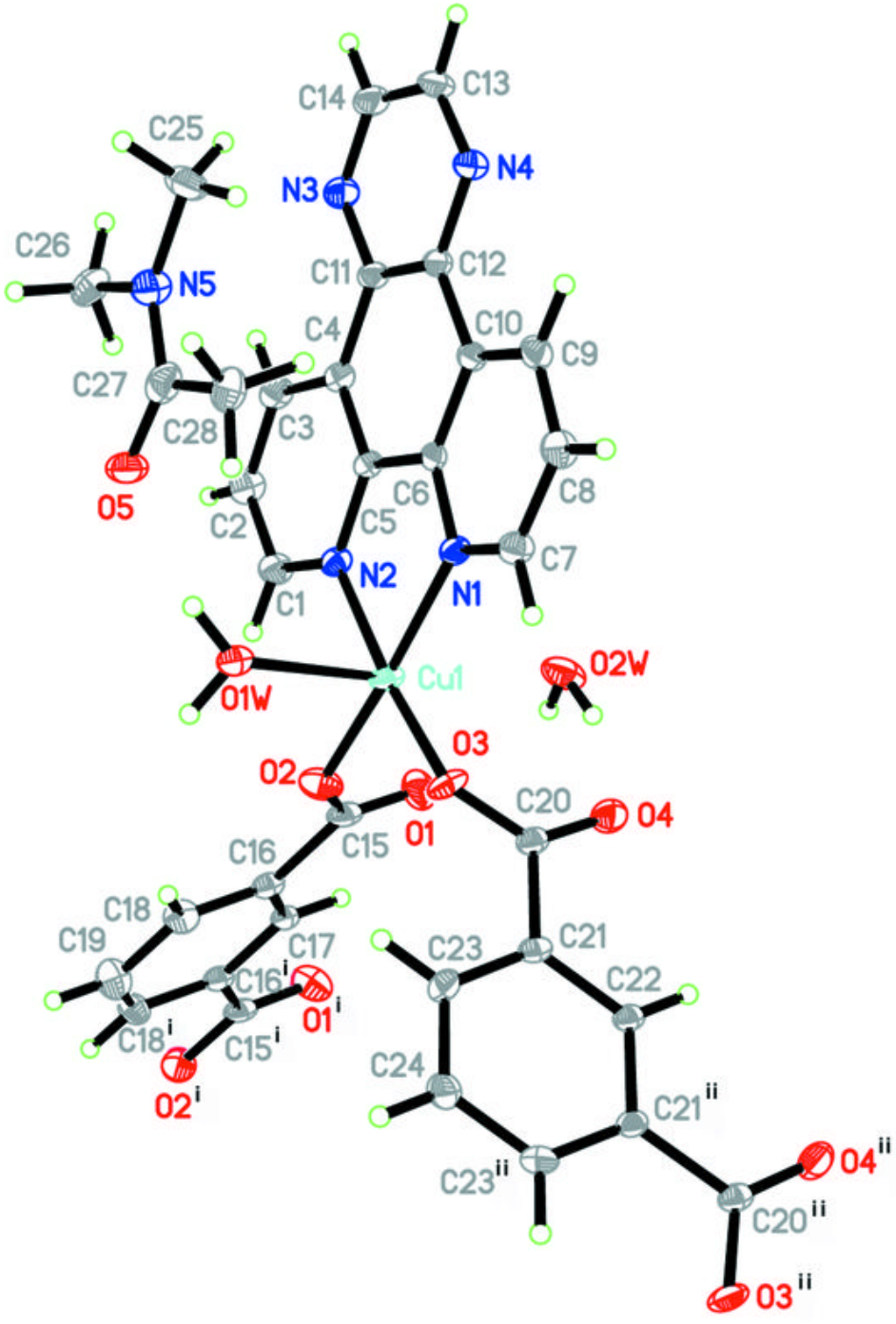
C14
C13
C25
N3
N4
C26
C11
C12
N5
C4
C10
C9
C27
C28
C3
C6
C8
O5
C2
C5
C7
N2
N1
C1
O1W
Cu1
O2W
O3
O2
C20
O4
O1
C15
C16
C18
C19
C17
C23
C21
C16i
C22
O1i
C18i
C15i
C24
O2i
C21ii
O4ii
C23ii
C20ii
O3ii

**Fig. 2**