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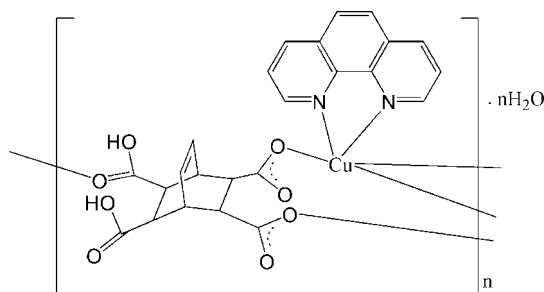
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.065; data-to-parameter ratio = 13.7.

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).

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

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supplementary materials

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

Poly[[(μ_3 -5,6-dicarboxybicyclo[2.2.2]oct-7-ene-2,3-dicarboxylato)(1,10-phenanthroline)copper(II)] monohydrate]

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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

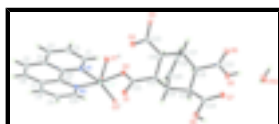


Fig. 1. Part of the polymeric structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (i) $x - 1, y, z$; (ii) $2 - x, y - 1/2, 2 - z$.

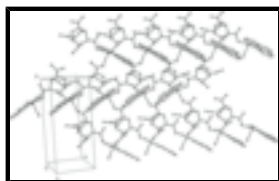


Fig. 2. View of a zigzag sheet structure in the title compound.

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) |

supplementary materials

| | | | | |
|------|-------------|---------------|---------------|-------------|
| 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

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|-------------|-------------|--------------------------|-------------|
| 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 |

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|-----------------|-------------|---|--------------|
| 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

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|-----------------|-------------|------------------------------|--------------|
| 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 ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| 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. 1

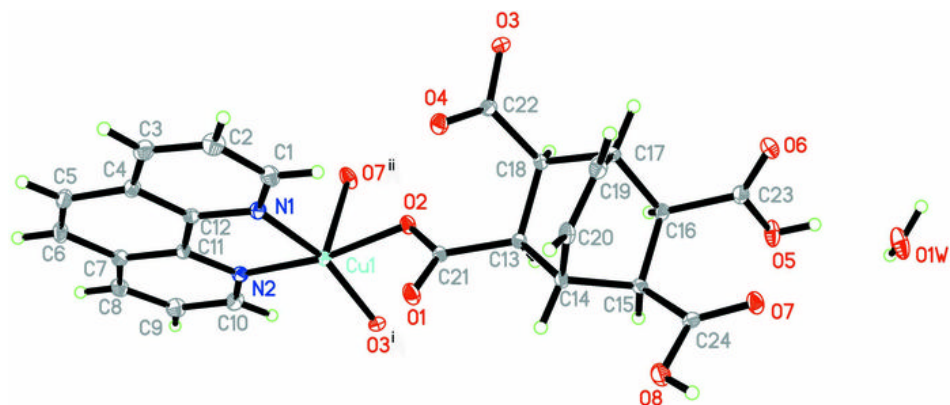


Fig. 2

