

μ -Oxalato-bis[(2,2'-bipyridyl)copper(II)] bis(perchlorate) dimethylformamide disolvate monohydrate

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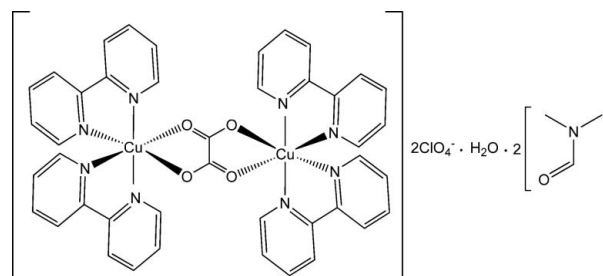
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; disorder in solvent or counterion; R factor = 0.047; wR factor = 0.129; data-to-parameter ratio = 13.9.

The title compound, $[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_7\text{NO} \cdot \text{H}_2\text{O}$, contains doubly charged centrosymmetric dinuclear oxalato-bridged copper(II) complex cations, perchlorate anions, and DMF and water solvate molecules. In the complex cation, the oxalate ligand is coordinated in a bis-bidentate bridging mode to the Cu atoms. Each Cu atom has a distorted tetragonal-bipyramidal environment, being coordinated by two N atoms of the two chelating bipy ligands and two O atoms of the doubly deprotonated oxalate anion. Pairs of perchlorate anions and water molecules are linked into rectangles by $\text{O}-\text{H} \cdots \text{O}$ bonds in which the perchlorate O atoms act as acceptors and the water molecules as donors. Methyl groups of the DMF solvent molecule are disordered over two sites with occupancies of 0.453 (7):0.547 (7), and the water molecule is half-occupied.

Related literature

For use of oxalic acid and its derivatives in molecular magnetism and supramolecular chemistry, see: Kahn (1987); Ojima & Nonoyama (1988); Fritsky *et al.* (1998); Świątek-Kozłowska *et al.* (2000). For use of oxalic acid for the preparation of mixed-ligand polynuclear complexes, see: Strotmeyer *et al.* (2003). For related structures, see: Krämer & Fritsky (2000); Kovbasyuk *et al.* (2004); Wörl *et al.* (2005); Tomyn *et al.* (2007); Moroz *et al.* (2010).



Experimental

Crystal data

$[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_7\text{NO} \cdot \text{H}_2\text{O}$
 $M_r = 1202.94$
 Triclinic, $P\bar{1}$
 $a = 9.6872$ (5) Å
 $b = 11.0080$ (8) Å
 $c = 12.2449$ (5) Å
 $\alpha = 97.928$ (3)°
 $\beta = 99.565$ (2)°
 $\gamma = 91.924$ (2)°
 $V = 1273.16$ (12) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.02$ mm⁻¹
 $T = 100$ K
 $0.23 \times 0.12 \times 0.08$ mm

Data collection

Bruker Kappa APEXII DUO CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.802$, $T_{\max} = 0.923$
 10051 measured reflections
 4993 independent reflections
 3955 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.129$
 $S = 1.04$
 4993 reflections
 359 parameters
 27 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.70$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|-------|--------------|--------------|----------------|
| $\text{O1W}-\text{H1W} \cdots \text{O5}^i$ | 0.91 | 2.45 | 3.311 (13) | 159 |
| $\text{O1W}-\text{H2W} \cdots \text{O5}$ | 0.85 | 2.04 | 2.882 (14) | 169 |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Bradenburg, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2192).

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supplementary materials

Acta Cryst. (2010). E66, m1101-m1102 [doi:10.1107/S1600536810031569]

μ -Oxalato-bis[(2,2'-bipyridyl)copper(II)] bis(perchlorate) dimethylformamide disolvate monohydrate

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Comment

Oxalic acid and its amide derivatives are widely used in molecular magnetism and supramolecular chemistry for preparation of various bi- and polynuclear complexes as well as exchange clusters of high nuclearity (Kahn, 1987; Ojima & Nonoyama, 1988; Fritsky *et al.*, 1998; Świątek-Kozłowska *et al.*, 2000). Use of additional bridging ligands sometimes results in increase of nuclearity of the target mixed ligands compounds (Strotmeyer *et al.*, 2003). However, use of this synthetic strategy is often restricted by formation of complex species containing only one of the used bridging ligands. Herein we report a compound (I) isolated as a result of an attempt to obtain a mixed ligand complex containing both oxalate and pyridine-2-hydroxamate ligands.

In (I), the Cu atom has a distorted tetragonal-bipyramidal environment, with one oxygen atom of the oxalate (O2), three nitrogen atoms of the 2,2'-bipyridine ligand (N1, N2 and N4) occupying the base of the pyramid, and the second oxygen atom of the oxalate (O1) and one of the bipyridine nitrogen atoms (N3) in the apical positions (Fig. 1). The planar μ_4 -oxalato group lies in a center of symmetry and bridges the two copper atoms in a bis(chelating) mode, each copper atom being bound to two oxygens from the two different carboxylic groups. The Cu...Cu separation in the dimer is 5.6032 (9) Å which is slightly longer than the intermetallic separation observed in a related μ_4 -oxalato-bridged dicopper complex with (1-(pyridin-2-yl)ethylidene)hydrazine (5.449 (1) Å) (Tomyń *et al.*, 2007). The C-N and C-C bond lengths in the 2,2'-bipyridine ligands are normal for 2-substituted pyridine derivatives (Krämer *et al.*, 2000; Kovbasyuk *et al.*, 2004; Wörl *et al.*, 2005; Moroz *et al.*, 2010).

In the crystal packing, the dimeric complex cations are organized in layers disposed parallel to the xy plane. The neighboring cations are linked by stacking interactions between the pyridine rings (both along x and y directions) and by van der Waals forces. The perchlorate anions and solvate water molecules are disposed between the cationic layers. Two pairs of the translational perchlorate anions and water molecules form rectangles due to H-bonds where perchlorate O atoms act as acceptors and H₂O molecules as donors (Fig. 2, Table 1).

Experimental

Cu(ClO₄)₂·6H₂O (0.371 g, 1 mmol) was dissolved in water (5 ml) and added to the dimethylformamide solution of pyridine-2-hydroxamic acid (0.138 g, 1 mmol) and 2,2'-bipyridine (0.156 g, 1 mmol), and then a powder of K₂C₂O₄·H₂O (0.092 g, 0.5 mmol) was added to the obtained solution. The resulting mixture was being stirred at 60 °C during 15 min and filtered. Turquoise crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether vapour to the resulting solution at room temperature within 72 hours. They were filtered off and washed with diethyl ether. Yield: 57%.

Refinement

Methyl groups of the dimethylformamide solvent molecule were disordered over two sites with occupancies 0.45/0.55. The N-C distances in the dimethylformamide molecules were restrained to be similar and the anisotropic displacement parameters of the methyl carbons were constrained to be equal. The water of crystallization was refined with occupancy of 0.5. The H₂O hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with $U_{\text{iso}} = 1.5 U_{\text{eq}}(\text{parent atom})$. Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C—H = 0.95-0.98 Å, and $U_{\text{iso}} = 1.2-1.5 U_{\text{eq}}(\text{parent atom})$. The highest peak is located 0.58 Å from atom C22B and the deepest hole is located 0.60 Å from atom O7.

Figures

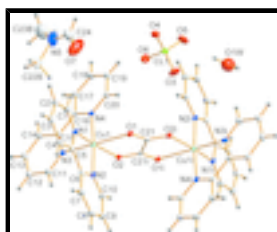


Fig. 1. A view of compound (1), with displacement ellipsoids shown at the 30% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i)1-x,1-y,1-z].

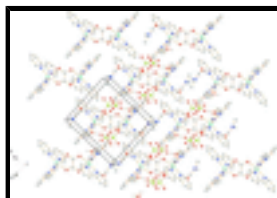


Fig. 2. A packing diagram of the title compound. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

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Crystal data

| | |
|--|---|
| $[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_7\text{NO} \cdot \text{H}_2\text{O}$ | $Z = 1$ |
| $M_r = 1202.94$ | $F(000) = 618$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.569 \text{ Mg m}^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 9.6872 (5) \text{ \AA}$ | Cell parameters from 3860 reflections |
| $b = 11.0080 (8) \text{ \AA}$ | $\theta = 2.3\text{--}27.4^\circ$ |
| $c = 12.2449 (5) \text{ \AA}$ | $\mu = 1.02 \text{ mm}^{-1}$ |
| $\alpha = 97.928 (3)^\circ$ | $T = 100 \text{ K}$ |
| $\beta = 99.565 (2)^\circ$ | Block, turquoise |
| $\gamma = 91.924 (2)^\circ$ | $0.23 \times 0.12 \times 0.08 \text{ mm}$ |
| $V = 1273.16 (12) \text{ \AA}^3$ | |

Data collection

Bruker Kappa APEXII DUO CCD 4993 independent reflections

diffractometer
 Radiation source: fine-focus sealed tube 3955 reflections with $I > 2\sigma(I)$
 curved graphite crystal $R_{\text{int}} = 0.023$
 Detector resolution: 16 pixels mm^{-1} $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 1.7^\circ$
 φ scans and ω scans with κ offset $h = -11 \rightarrow 11$
 Absorption correction: multi-scan (*SADABS*; Bruker, 2009) $k = -13 \rightarrow 13$
 $T_{\text{min}} = 0.802$, $T_{\text{max}} = 0.923$ $l = -10 \rightarrow 15$
 10051 measured reflections

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
 Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.047$ Hydrogen site location: inferred from neighbouring sites
 $wR(F^2) = 0.129$ H-atom parameters constrained
 $S = 1.04$ $w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 2.0663P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 4993 reflections $(\Delta/\sigma)_{\text{max}} < 0.001$
 359 parameters $\Delta\rho_{\text{max}} = 1.43 \text{ e } \text{\AA}^{-3}$
 27 restraints $\Delta\rho_{\text{min}} = -0.70 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|-------------|-------------|----------------------------------|-----------|
| Cu1 | 0.29558 (4) | 0.30820 (4) | 0.41931 (4) | 0.01694 (15) | |
| Cl1 | 0.71283 (9) | 0.33716 (9) | 0.90518 (8) | 0.0256 (2) | |
| O1 | 0.5313 (3) | 0.3455 (2) | 0.5049 (2) | 0.0206 (6) | |
| O2 | 0.3249 (2) | 0.4898 (2) | 0.4286 (2) | 0.0176 (5) | |
| O3 | 0.7943 (4) | 0.3548 (3) | 0.8209 (3) | 0.0517 (9) | |
| O4 | 0.7375 (3) | 0.2198 (3) | 0.9423 (3) | 0.0351 (7) | |
| O5 | 0.7470 (4) | 0.4320 (3) | 0.9976 (3) | 0.0534 (10) | |
| O6 | 0.5683 (3) | 0.3377 (4) | 0.8567 (3) | 0.0523 (10) | |
| O7 | 0.3074 (6) | 0.0419 (7) | 0.7731 (7) | 0.138 (3) | |

supplementary materials

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|------|-------------|-------------|-------------|-------------|-----------|
| N1 | 0.3182 (3) | 0.1260 (3) | 0.4105 (3) | 0.0199 (7) | |
| N2 | 0.3572 (3) | 0.2758 (3) | 0.2693 (3) | 0.0176 (6) | |
| N3 | 0.0654 (3) | 0.3071 (3) | 0.3574 (3) | 0.0190 (6) | |
| N4 | 0.2160 (3) | 0.3330 (3) | 0.5640 (3) | 0.0177 (6) | |
| N5 | 0.0955 (5) | 0.0617 (5) | 0.7989 (5) | 0.0720 (17) | |
| C1 | 0.2978 (4) | 0.0562 (4) | 0.4883 (4) | 0.0293 (9) | |
| H1 | 0.2670 | 0.0932 | 0.5542 | 0.035* | |
| C2 | 0.3199 (4) | -0.0685 (4) | 0.4759 (4) | 0.0321 (10) | |
| H2 | 0.3052 | -0.1160 | 0.5325 | 0.039* | |
| C3 | 0.3636 (4) | -0.1221 (3) | 0.3802 (4) | 0.0287 (9) | |
| H3 | 0.3776 | -0.2076 | 0.3694 | 0.034* | |
| C4 | 0.3870 (4) | -0.0508 (3) | 0.3001 (4) | 0.0256 (8) | |
| H4 | 0.4179 | -0.0863 | 0.2338 | 0.031* | |
| C5 | 0.3646 (3) | 0.0738 (3) | 0.3182 (3) | 0.0186 (7) | |
| C6 | 0.3871 (3) | 0.1588 (3) | 0.2378 (3) | 0.0180 (7) | |
| C7 | 0.4363 (4) | 0.1248 (4) | 0.1392 (3) | 0.0269 (9) | |
| H7 | 0.4560 | 0.0418 | 0.1176 | 0.032* | |
| C8 | 0.4568 (4) | 0.2125 (4) | 0.0723 (3) | 0.0292 (9) | |
| H8 | 0.4916 | 0.1906 | 0.0045 | 0.035* | |
| C9 | 0.4265 (4) | 0.3320 (4) | 0.1045 (3) | 0.0267 (9) | |
| H9 | 0.4406 | 0.3939 | 0.0599 | 0.032* | |
| C10 | 0.3753 (4) | 0.3601 (3) | 0.2029 (3) | 0.0233 (8) | |
| H10 | 0.3520 | 0.4421 | 0.2245 | 0.028* | |
| C11 | -0.0050 (4) | 0.2868 (4) | 0.2522 (3) | 0.0259 (8) | |
| H11 | 0.0470 | 0.2737 | 0.1928 | 0.031* | |
| C12 | -0.1495 (4) | 0.2839 (4) | 0.2259 (4) | 0.0279 (9) | |
| H12 | -0.1961 | 0.2686 | 0.1503 | 0.033* | |
| C13 | -0.2244 (4) | 0.3038 (4) | 0.3131 (4) | 0.0275 (9) | |
| H13 | -0.3239 | 0.3025 | 0.2979 | 0.033* | |
| C14 | -0.1538 (4) | 0.3256 (3) | 0.4223 (3) | 0.0210 (8) | |
| H14 | -0.2038 | 0.3397 | 0.4829 | 0.025* | |
| C15 | -0.0077 (4) | 0.3266 (3) | 0.4419 (3) | 0.0177 (7) | |
| C16 | 0.0767 (4) | 0.3479 (3) | 0.5566 (3) | 0.0177 (7) | |
| C17 | 0.0176 (4) | 0.3815 (3) | 0.6520 (3) | 0.0233 (8) | |
| H17 | -0.0802 | 0.3919 | 0.6458 | 0.028* | |
| C18 | 0.1027 (4) | 0.3992 (4) | 0.7553 (3) | 0.0274 (9) | |
| H18 | 0.0641 | 0.4226 | 0.8209 | 0.033* | |
| C19 | 0.2450 (4) | 0.3828 (4) | 0.7632 (3) | 0.0273 (9) | |
| H19 | 0.3052 | 0.3939 | 0.8339 | 0.033* | |
| C20 | 0.2973 (4) | 0.3496 (3) | 0.6654 (3) | 0.0218 (8) | |
| H20 | 0.3947 | 0.3381 | 0.6703 | 0.026* | |
| C21 | 0.5591 (4) | 0.4576 (3) | 0.5219 (3) | 0.0168 (7) | |
| C22A | 0.0103 (10) | 0.0664 (11) | 0.7051 (11) | 0.049 (2) | 0.453 (7) |
| H22A | -0.0851 | 0.0770 | 0.7202 | 0.074* | 0.453 (7) |
| H22B | 0.0119 | -0.0101 | 0.6540 | 0.074* | 0.453 (7) |
| H22C | 0.0402 | 0.1359 | 0.6707 | 0.074* | 0.453 (7) |
| C23A | 0.075 (2) | 0.1244 (19) | 0.9138 (14) | 0.107 (4) | 0.453 (7) |
| H23A | -0.0240 | 0.1429 | 0.9113 | 0.161* | 0.453 (7) |
| H23B | 0.1336 | 0.2010 | 0.9343 | 0.161* | 0.453 (7) |

| | | | | | |
|------|--------------|-------------|-------------|-----------|-----------|
| H23C | 0.1010 | 0.0697 | 0.9696 | 0.161* | 0.453 (7) |
| C22B | 0.0510 (8) | 0.0191 (9) | 0.6636 (8) | 0.049 (2) | 0.547 (7) |
| H22D | -0.0497 | 0.0275 | 0.6410 | 0.074* | 0.547 (7) |
| H22E | 0.0726 | -0.0668 | 0.6447 | 0.074* | 0.547 (7) |
| H22F | 0.1036 | 0.0711 | 0.6241 | 0.074* | 0.547 (7) |
| C23B | -0.0322 (15) | 0.1000 (16) | 0.8376 (15) | 0.107 (4) | 0.547 (7) |
| H23D | -0.1106 | 0.0875 | 0.7745 | 0.161* | 0.547 (7) |
| H23E | -0.0206 | 0.1872 | 0.8694 | 0.161* | 0.547 (7) |
| H23F | -0.0517 | 0.0512 | 0.8950 | 0.161* | 0.547 (7) |
| C24 | 0.2302 (8) | 0.0497 (10) | 0.8262 (7) | 0.100 (3) | |
| H24 | 0.2637 | 0.0475 | 0.9034 | 0.121* | |
| O1W | 0.9215 (13) | 0.6412 (13) | 0.9750 (10) | 0.119 (4) | 0.50 |
| H1W | 1.0104 | 0.6270 | 0.9637 | 0.179* | 0.50 |
| H2W | 0.8765 | 0.5737 | 0.9756 | 0.179* | 0.50 |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Cu1 | 0.0187 (2) | 0.0152 (2) | 0.0193 (3) | 0.00275 (16) | 0.00795 (17) | 0.00502 (17) |
| Cl1 | 0.0245 (5) | 0.0333 (5) | 0.0202 (5) | 0.0044 (4) | 0.0052 (4) | 0.0060 (4) |
| O1 | 0.0211 (13) | 0.0159 (13) | 0.0269 (15) | 0.0031 (10) | 0.0067 (11) | 0.0074 (11) |
| O2 | 0.0161 (12) | 0.0166 (12) | 0.0217 (14) | 0.0036 (9) | 0.0059 (10) | 0.0043 (10) |
| O3 | 0.059 (2) | 0.058 (2) | 0.049 (2) | 0.0059 (18) | 0.0366 (18) | 0.0171 (18) |
| O4 | 0.0452 (17) | 0.0316 (16) | 0.0297 (17) | 0.0101 (13) | 0.0065 (14) | 0.0069 (13) |
| O5 | 0.091 (3) | 0.0350 (18) | 0.0285 (18) | 0.0096 (18) | -0.0034 (18) | -0.0029 (15) |
| O6 | 0.0277 (16) | 0.072 (3) | 0.062 (2) | 0.0046 (16) | -0.0021 (16) | 0.035 (2) |
| O7 | 0.070 (4) | 0.139 (6) | 0.236 (9) | 0.031 (4) | 0.044 (5) | 0.107 (6) |
| N1 | 0.0209 (15) | 0.0146 (15) | 0.0249 (17) | -0.0006 (12) | 0.0043 (13) | 0.0058 (13) |
| N2 | 0.0170 (14) | 0.0155 (14) | 0.0210 (16) | 0.0020 (11) | 0.0037 (12) | 0.0039 (12) |
| N3 | 0.0193 (15) | 0.0214 (16) | 0.0181 (16) | 0.0022 (12) | 0.0057 (12) | 0.0058 (13) |
| N4 | 0.0165 (14) | 0.0169 (15) | 0.0214 (17) | 0.0007 (11) | 0.0050 (12) | 0.0070 (13) |
| N5 | 0.038 (3) | 0.060 (3) | 0.117 (5) | 0.011 (2) | 0.032 (3) | -0.015 (3) |
| C1 | 0.038 (2) | 0.023 (2) | 0.030 (2) | -0.0007 (17) | 0.0105 (18) | 0.0074 (17) |
| C2 | 0.039 (2) | 0.021 (2) | 0.036 (3) | -0.0037 (17) | 0.0019 (19) | 0.0133 (18) |
| C3 | 0.031 (2) | 0.0142 (18) | 0.037 (2) | 0.0020 (16) | -0.0067 (18) | 0.0056 (17) |
| C4 | 0.0266 (19) | 0.0194 (19) | 0.029 (2) | 0.0046 (15) | 0.0007 (17) | -0.0002 (16) |
| C5 | 0.0144 (16) | 0.0192 (18) | 0.0200 (19) | -0.0001 (13) | -0.0033 (14) | 0.0030 (15) |
| C6 | 0.0130 (16) | 0.0188 (18) | 0.0208 (19) | 0.0018 (13) | 0.0003 (14) | 0.0006 (15) |
| C7 | 0.032 (2) | 0.025 (2) | 0.024 (2) | 0.0060 (16) | 0.0081 (17) | -0.0021 (16) |
| C8 | 0.032 (2) | 0.036 (2) | 0.021 (2) | 0.0026 (18) | 0.0107 (17) | 0.0004 (18) |
| C9 | 0.029 (2) | 0.028 (2) | 0.025 (2) | -0.0008 (16) | 0.0087 (17) | 0.0088 (17) |
| C10 | 0.0278 (19) | 0.0192 (18) | 0.025 (2) | 0.0029 (15) | 0.0094 (16) | 0.0057 (16) |
| C11 | 0.0257 (19) | 0.030 (2) | 0.023 (2) | 0.0024 (16) | 0.0068 (16) | 0.0051 (17) |
| C12 | 0.027 (2) | 0.032 (2) | 0.024 (2) | -0.0016 (16) | -0.0008 (16) | 0.0056 (17) |
| C13 | 0.0189 (18) | 0.030 (2) | 0.033 (2) | 0.0015 (16) | 0.0027 (16) | 0.0049 (18) |
| C14 | 0.0208 (17) | 0.0181 (18) | 0.026 (2) | 0.0016 (14) | 0.0077 (15) | 0.0051 (15) |
| C15 | 0.0198 (17) | 0.0132 (16) | 0.0215 (19) | 0.0017 (13) | 0.0072 (15) | 0.0032 (14) |
| C16 | 0.0188 (17) | 0.0148 (17) | 0.0213 (19) | -0.0001 (13) | 0.0068 (14) | 0.0055 (14) |

supplementary materials

| | | | | | | |
|------|-------------|-------------|-------------|--------------|-------------|-------------|
| C17 | 0.0205 (18) | 0.0253 (19) | 0.026 (2) | 0.0008 (15) | 0.0103 (16) | 0.0030 (16) |
| C18 | 0.028 (2) | 0.034 (2) | 0.023 (2) | 0.0019 (17) | 0.0125 (17) | 0.0038 (17) |
| C19 | 0.026 (2) | 0.035 (2) | 0.022 (2) | -0.0014 (17) | 0.0053 (16) | 0.0073 (17) |
| C20 | 0.0188 (17) | 0.0252 (19) | 0.023 (2) | 0.0006 (15) | 0.0053 (15) | 0.0062 (16) |
| C21 | 0.0198 (17) | 0.0185 (18) | 0.0159 (18) | 0.0044 (14) | 0.0093 (14) | 0.0070 (14) |
| C22A | 0.011 (3) | 0.039 (4) | 0.098 (6) | 0.002 (3) | 0.005 (3) | 0.021 (4) |
| C23A | 0.083 (6) | 0.126 (7) | 0.107 (7) | 0.019 (5) | 0.019 (5) | -0.007 (6) |
| C22B | 0.011 (3) | 0.039 (4) | 0.098 (6) | 0.002 (3) | 0.005 (3) | 0.021 (4) |
| C23B | 0.083 (6) | 0.126 (7) | 0.107 (7) | 0.019 (5) | 0.019 (5) | -0.007 (6) |
| C24 | 0.050 (4) | 0.178 (10) | 0.066 (5) | -0.029 (5) | -0.004 (4) | 0.017 (5) |
| O1S | 0.095 (8) | 0.155 (12) | 0.110 (10) | -0.004 (8) | 0.015 (7) | 0.032 (9) |

Geometric parameters (Å, °)

| | | | |
|---------------------|------------|----------------------|-----------|
| Cu1—O2 | 1.995 (2) | C8—H8 | 0.9500 |
| Cu1—N2 | 2.015 (3) | C9—C10 | 1.378 (5) |
| Cu1—N1 | 2.015 (3) | C9—H9 | 0.9500 |
| Cu1—N4 | 2.036 (3) | C10—H10 | 0.9500 |
| Cu1—N3 | 2.232 (3) | C11—C12 | 1.381 (5) |
| Cu1—O1 | 2.346 (3) | C11—H11 | 0.9500 |
| Cl1—O5 | 1.417 (3) | C12—C13 | 1.383 (6) |
| Cl1—O6 | 1.428 (3) | C12—H12 | 0.9500 |
| Cl1—O3 | 1.428 (3) | C13—C14 | 1.382 (6) |
| Cl1—O4 | 1.442 (3) | C13—H13 | 0.9500 |
| O1—C21 | 1.236 (4) | C14—C15 | 1.395 (5) |
| O2—C21 ⁱ | 1.265 (4) | C14—H14 | 0.9500 |
| O7—C24 | 1.065 (9) | C15—C16 | 1.486 (5) |
| N1—C1 | 1.339 (5) | C16—C17 | 1.395 (5) |
| N1—C5 | 1.348 (5) | C17—C18 | 1.375 (6) |
| N2—C10 | 1.340 (5) | C17—H17 | 0.9500 |
| N2—C6 | 1.348 (4) | C18—C19 | 1.384 (5) |
| N3—C11 | 1.339 (5) | C18—H18 | 0.9500 |
| N3—C15 | 1.346 (5) | C19—C20 | 1.385 (5) |
| N4—C20 | 1.340 (5) | C19—H19 | 0.9500 |
| N4—C16 | 1.354 (4) | C20—H20 | 0.9500 |
| N5—C22A | 1.313 (11) | C21—O2 ⁱ | 1.265 (4) |
| N5—C24 | 1.305 (9) | C21—C21 ⁱ | 1.573 (7) |
| N5—C23B | 1.463 (14) | C22A—H22A | 0.9800 |
| N5—C23A | 1.527 (14) | C22A—H22B | 0.9800 |
| N5—C22B | 1.631 (11) | C22A—H22C | 0.9800 |
| C1—C2 | 1.387 (6) | C23A—H23A | 0.9800 |
| C1—H1 | 0.9500 | C23A—H23B | 0.9800 |
| C2—C3 | 1.375 (6) | C23A—H23C | 0.9800 |
| C2—H2 | 0.9500 | C22B—H22D | 0.9800 |
| C3—C4 | 1.379 (6) | C22B—H22E | 0.9800 |
| C3—H3 | 0.9500 | C22B—H22F | 0.9800 |
| C4—C5 | 1.390 (5) | C23B—H23D | 0.9800 |
| C4—H4 | 0.9500 | C23B—H23E | 0.9800 |

| | | | |
|--------------------------|-------------|---------------------------------------|-----------|
| C5—C6 | 1.485 (5) | C23B—H23F | 0.9800 |
| C6—C7 | 1.380 (5) | C24—H24 | 0.9500 |
| C7—C8 | 1.379 (6) | O1W—H1W | 0.9100 |
| C7—H7 | 0.9500 | O1W—H2W | 0.8500 |
| C8—C9 | 1.377 (6) | | |
| O2—Cu1—N2 | 92.86 (11) | C8—C9—C10 | 118.6 (4) |
| O2—Cu1—N1 | 165.61 (11) | C8—C9—H9 | 120.7 |
| N2—Cu1—N1 | 80.78 (12) | C10—C9—H9 | 120.7 |
| O2—Cu1—N4 | 89.79 (11) | N2—C10—C9 | 122.3 (4) |
| N2—Cu1—N4 | 174.69 (12) | N2—C10—H10 | 118.8 |
| N1—Cu1—N4 | 97.65 (12) | C9—C10—H10 | 118.8 |
| O2—Cu1—N3 | 93.94 (10) | N3—C11—C12 | 123.2 (4) |
| N2—Cu1—N3 | 97.73 (11) | N3—C11—H11 | 118.4 |
| N1—Cu1—N3 | 99.68 (12) | C12—C11—H11 | 118.4 |
| N4—Cu1—N3 | 77.48 (11) | C11—C12—C13 | 118.1 (4) |
| O2—Cu1—O1 | 77.12 (9) | C11—C12—H12 | 121.0 |
| N2—Cu1—O1 | 89.30 (11) | C13—C12—H12 | 121.0 |
| N1—Cu1—O1 | 89.83 (10) | C14—C13—C12 | 119.7 (4) |
| N4—Cu1—O1 | 95.78 (10) | C14—C13—H13 | 120.2 |
| N3—Cu1—O1 | 168.94 (10) | C12—C13—H13 | 120.2 |
| O5—C11—O6 | 110.2 (2) | C13—C14—C15 | 118.8 (4) |
| O5—C11—O3 | 110.4 (2) | C13—C14—H14 | 120.6 |
| O6—C11—O3 | 107.9 (2) | C15—C14—H14 | 120.6 |
| O5—C11—O4 | 109.5 (2) | N3—C15—C14 | 121.6 (3) |
| O6—C11—O4 | 108.4 (2) | N3—C15—C16 | 115.9 (3) |
| O3—C11—O4 | 110.2 (2) | C14—C15—C16 | 122.5 (3) |
| C21—O1—Cu1 | 108.6 (2) | N4—C16—C17 | 121.1 (3) |
| C21 ⁱ —O2—Cu1 | 119.4 (2) | N4—C16—C15 | 116.2 (3) |
| C1—N1—C5 | 118.8 (3) | C17—C16—C15 | 122.7 (3) |
| C1—N1—Cu1 | 126.4 (3) | C18—C17—C16 | 119.2 (3) |
| C5—N1—Cu1 | 114.7 (2) | C18—C17—H17 | 120.4 |
| C10—N2—C6 | 119.1 (3) | C16—C17—H17 | 120.4 |
| C10—N2—Cu1 | 125.8 (3) | C17—C18—C19 | 119.8 (4) |
| C6—N2—Cu1 | 115.0 (2) | C17—C18—H18 | 120.1 |
| C11—N3—C15 | 118.6 (3) | C19—C18—H18 | 120.1 |
| C11—N3—Cu1 | 129.3 (3) | C20—C19—C18 | 118.3 (4) |
| C15—N3—Cu1 | 112.0 (2) | C20—C19—H19 | 120.9 |
| C20—N4—C16 | 119.0 (3) | C18—C19—H19 | 120.9 |
| C20—N4—Cu1 | 122.7 (2) | N4—C20—C19 | 122.7 (3) |
| C16—N4—Cu1 | 117.9 (2) | N4—C20—H20 | 118.7 |
| C22A—N5—C24 | 134.7 (8) | C19—C20—H20 | 118.7 |
| C22A—N5—C23B | 78.1 (9) | O1—C21—O2 ⁱ | 125.4 (3) |
| C24—N5—C23B | 146.3 (9) | O1—C21—C21 ⁱ | 117.5 (4) |
| C22A—N5—C23A | 125.4 (9) | O2 ⁱ —C21—C21 ⁱ | 117.1 (4) |
| C24—N5—C23A | 96.1 (9) | N5—C22A—H22A | 109.4 |
| C23B—N5—C23A | 49.9 (9) | N5—C22A—H22B | 109.5 |
| C24—N5—C22B | 108.0 (6) | H22A—C22A—H22B | 109.5 |
| C23B—N5—C22B | 105.5 (9) | N5—C22A—H22C | 109.5 |

supplementary materials

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|--------------|-----------|----------------|-----------|
| C23A—N5—C22B | 154.7 (8) | H22A—C22A—H22C | 109.5 |
| N1—C1—C2 | 122.2 (4) | H22B—C22A—H22C | 109.5 |
| N1—C1—H1 | 118.9 | N5—C23A—H23A | 109.5 |
| C2—C1—H1 | 118.9 | N5—C23A—H23B | 109.4 |
| C3—C2—C1 | 118.8 (4) | H23A—C23A—H23B | 109.5 |
| C3—C2—H2 | 120.6 | N5—C23A—H23C | 109.5 |
| C1—C2—H2 | 120.6 | H23A—C23A—H23C | 109.5 |
| C2—C3—C4 | 119.6 (4) | H23B—C23A—H23C | 109.5 |
| C2—C3—H3 | 120.2 | N5—C22B—H22D | 109.5 |
| C4—C3—H3 | 120.2 | N5—C22B—H22E | 109.5 |
| C3—C4—C5 | 118.7 (4) | H22D—C22B—H22E | 109.5 |
| C3—C4—H4 | 120.6 | N5—C22B—H22F | 109.5 |
| C5—C4—H4 | 120.6 | H22D—C22B—H22F | 109.5 |
| N1—C5—C4 | 121.8 (3) | H22E—C22B—H22F | 109.5 |
| N1—C5—C6 | 115.0 (3) | N5—C23B—H23D | 109.5 |
| C4—C5—C6 | 123.2 (4) | N5—C23B—H23E | 109.5 |
| N2—C6—C7 | 121.2 (3) | H23D—C23B—H23E | 109.5 |
| N2—C6—C5 | 114.4 (3) | N5—C23B—H23F | 109.4 |
| C7—C6—C5 | 124.4 (3) | H23D—C23B—H23F | 109.5 |
| C8—C7—C6 | 119.3 (4) | H23E—C23B—H23F | 109.5 |
| C8—C7—H7 | 120.3 | O7—C24—N5 | 128.6 (9) |
| C6—C7—H7 | 120.3 | O7—C24—H24 | 115.7 |
| C9—C8—C7 | 119.4 (4) | N5—C24—H24 | 115.7 |
| C9—C8—H8 | 120.3 | H1W—O1W—H2W | 110.2 |
| C7—C8—H8 | 120.3 | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| O1W—H1W \cdots O5 ⁱⁱ | 0.91 | 2.45 | 3.311 (13) | 159. |
| O1W—H2W \cdots O5 | 0.85 | 2.04 | 2.882 (14) | 169. |

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

Fig. 1

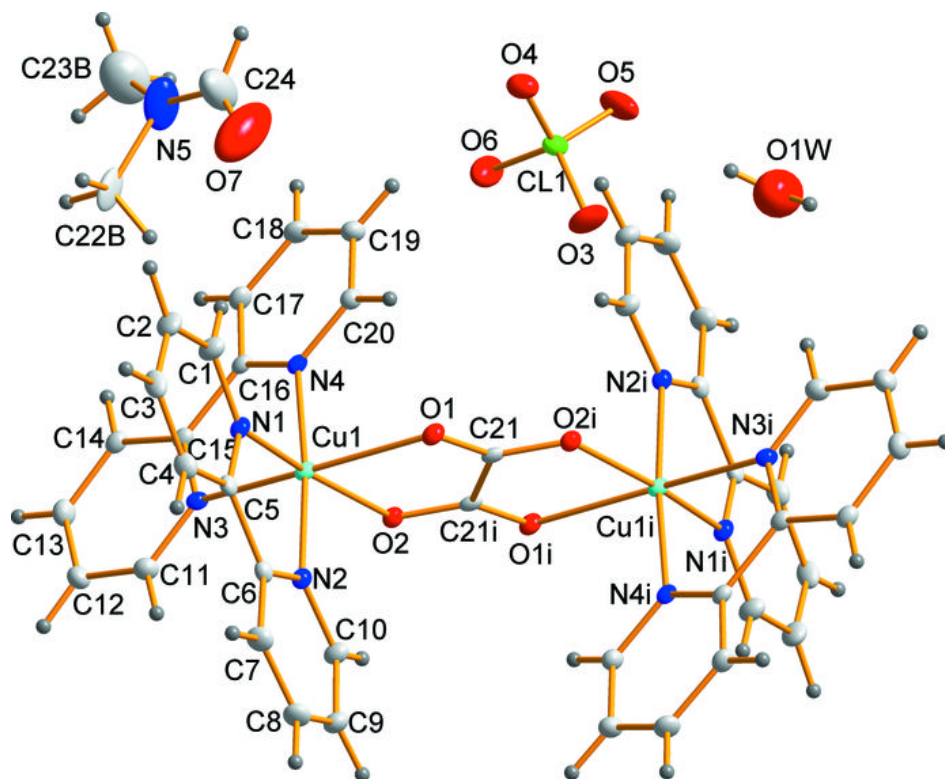


Fig. 2

