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# Bis(2,2′-bipyridyl)bromidocopper(II) bromide bromoacetic acid hemihydrate

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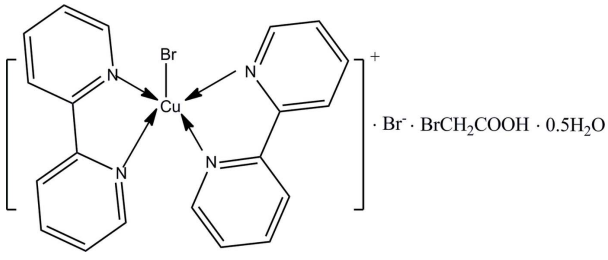
Key indicators: single-crystal X-ray study; $T$ = 273 K; mean $\sigma$(C–C) = 0.015 Å; disorder in solvent or counterion; $R$ factor = 0.067; $wR$ factor = 0.183; data-to-parameter ratio = 14.7.

In the title compound, $[CuBr(C_{10}H_8N_2)_2]Br\cdot BrCH_2COOH\cdot 0.5H_2O$, the $Cu^{II}$ ion is coordinated by four N atoms [Cu—N = 1.985 (6)–2.125 (7) Å] from two 2,2′-bipyridine ligand molecules and a bromide anion [Cu—Br = 2.471 (2) Å] in a distorted trigonal-bipyramidal geometry. Short centroid–centroid distances [3.762 (5) and 3.867 (5) Å] between the aromatic rings of neighbouring cations suggest the existence of $\pi$–$\pi$ interactions. Intermolecular O—H···Br hydrogen bonds and weak C—H···O and C—H···Br interactions consolidate the crystal packing.

## Related literature

For related structures, see: Hammond *et al.* (1999); Song *et al.* (2004).




## Experimental

### Crystal data

$[CuBr(C_{10}H_8N_2)_2]Br\cdot C_2H_3BrO_2\cdot 0.5H_2O$
$M_r$ = 683.69
Triclinic, $P\overline{1}$
$a$ = 8.580 (4) Å
$b$ = 12.125 (6) Å
$c$ = 13.212 (6) Å
$\alpha$ = 70.295 (9)°
$\beta$ = 81.427 (8)°
$\gamma$ = 76.669 (9)°
$V$ = 1255.3 (11) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 5.67 mm$^{-1}$
$T$ = 273 K
0.30 × 0.27 × 0.26 mm

### Data collection

Bruker or SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.281, $T_{max}$ = 0.320
6360 measured reflections
4384 independent reflections
2689 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.113

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.183
$S$ = 1.01
4384 reflections
299 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.10 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···Br3 | 0.82 | 2.34 | 3.129 (7) | 163 |
| O3—H3$A$···Br3 | 0.85 | 2.64 | 3.426 (11) | 154 |
| C14—H14···O1$^{i}$ | 0.93 | 2.46 | 3.254 (12) | 144 |
| C3—H3···O2$^{ii}$ | 0.93 | 2.60 | 3.374 (12) | 141 |
| C2—H2$B$···Br2$^{iii}$ | 0.97 | 2.88 | 3.815 (11) | 163 |
| C13—H13···Br1$^{iv}$ | 0.93 | 2.89 | 3.750 (10) | 154 |

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

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2644).

## References

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# supplementary materials

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# Bis(2,2'-bipyridyl)bromidocopper(II) bromide bromoacetic acid hemihydrate

**Y. Liu, J. Sun and X. Wang**

## Comment

Metal complexes with carboxylates are among the most investigated complexes in the field of coordination chemistry. In addition, metal-2,2'-bipyridine complexes and their derivatives have attracted much attention during recent decades because of their structural features (Hammond *et al.*, 1999; Song *et al.*, 2004). In this work, we present the crystal structure of the title compound (I) obtained from the bromoacetic acid and cupric acetate in the presence of co-ligand of 2,2'-bipyridine.

In (I) (Fig.1), the $Cu^{II}$ ion exhibits a five-coordinated trigonal bipyramidal geometry with four N atoms [Cu—N 1.985 (6)–2.125 (7) Å] from two 2,2'-bipyridine ligand molecules and a Br anion [Cu—Br 2.471 (2) Å]. Two N atoms and coordinated Br anion form an equatorial plane. The two rest coordinated N atoms occupy the apical positions with the N—Cu—N angle of 175.6 (3)/%. Intermolecular O—H···Br hydrogen bonds and weak C—H···O and C—H···Br interactions (Table1) consolidate the crystal packing, which exhibits relatively short intermolecular Br···Br contacts of 3.429 (3) Å.

## Experimental

The reaction was carried out by the solvothermal method. Bromoacetic acid (0.138 g,1 mmol) and cupric acetate(0.199 g, 1 mmol) and 2,2'-bipyridine(0.312 g, 2 mmol) were added to the airtight vessel with 1:2 ratio of ethanol and water. The resulting blue solution was filtered, and blue block-shaped crystals were obtained after several days. Yield 81%. Elemental analysis: calcd. for $C_{22}H_{20}Br_3Cu_1N_4O_{2.5}$: C 38.65, H 2.95, N 8.19; found: C 38.45, H 2.79, N 8.22. The elemental analyses were performed with PERKIN ELMER MODEL 2400 SERIES II.

## Refinement

All H atoms were geometrically positioned (C—H 0.93-0.97 Å, O—H 0.82-0.85 Å), abd refined as riding, with $U_{iso}$(H) = 1.2-1.5 $U_{eq}$(C, O).

## Figures

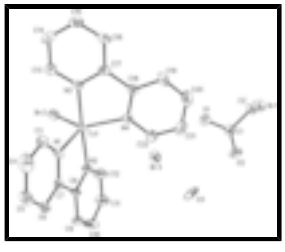


Fig. 1. The molecular structure of (I) showing the atomic numbering and 30% probability displacement ellipsoids. H atoms omitted for clarity.

## Bis(2,2'-bipyridyl)bromidocopper(II) bromide bromoacetic acid hemihydrate

*Crystal data*

| | |
|---|---|
| $[CuBr(C_{10}H_8N_2)_2]Br·C_2H_3BrO_2·0.5H_2O$ | $Z = 2$ |
| $M_r = 683.69$ | $F_{000} = 668$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.809$ Mg m$^{-3}$ |
| $a = 8.580$ (4) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 12.125$ (6) Å | Cell parameters from 1942 reflections |
| $c = 13.212$ (6) Å | $\theta = 2.5$–$26.3$º |
| $\alpha = 70.295$ (9)º | $\mu = 5.67$ mm$^{-1}$ |
| $\beta = 81.427$ (8)º | $T = 273$ K |
| $\gamma = 76.669$ (9)º | Block, blue |
| $V = 1255.3$ (11) Å$^3$ | 0.30 × 0.27 × 0.26 mm |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX diffractometer | 4384 independent reflections |
| Radiation source: fine-focus sealed tube | 2689 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.113$ |
| $T = 273$ K | $\theta_{max} = 25.1$º |
| phi and ω scans | $\theta_{min} = 1.8$º |
| Absorption correction: multi-scan (SADABS; Bruker, 2005) | $h = -8 \rightarrow 10$ |
| $T_{min} = 0.281$, $T_{max} = 0.320$ | $k = -11 \rightarrow 14$ |
| 6360 measured reflections | $l = -15 \rightarrow 15$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.067$ | H-atom parameters constrained |
| $wR(F^2) = 0.183$ | $w = 1/[\sigma^2(F_o^2) + (0.093P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.01$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 4384 reflections | $\Delta\rho_{max} = 1.20$ e Å$^{-3}$ |
| 299 parameters | $\Delta\rho_{min} = -1.10$ e Å$^{-3}$ |
| 3 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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.29541 (12) | 0.96050 (9) | 0.26233 (8) | 0.0355 (3) | |
| N1 | 0.2936 (8) | 1.0281 (6) | 0.3915 (5) | 0.0343 (17) | |
| N2 | 0.1969 (9) | 0.8397 (6) | 0.3826 (5) | 0.0396 (18) | |
| N3 | 0.4085 (8) | 1.0763 (6) | 0.1487 (5) | 0.0357 (17) | |
| N4 | 0.5077 (8) | 0.8468 (6) | 0.2359 (5) | 0.0335 (17) | |
| O1 | 0.5681 (9) | 0.4552 (7) | 0.1253 (6) | 0.072 (2) | |
| H1 | 0.4898 | 0.4612 | 0.1684 | 0.108* | |
| O2 | 0.6357 (9) | 0.2741 (8) | 0.2416 (6) | 0.090 (3) | |
| O3 | 0.4997 (16) | 0.4203 (11) | 0.4374 (10) | 0.057 (4) | 0.50 |
| H3A | 0.4339 | 0.4667 | 0.3920 | 0.068* | 0.50 |
| H3B | 0.5632 | 0.3711 | 0.4099 | 0.068* | 0.50 |
| Br1 | 0.96870 (13) | 0.40992 (10) | 0.14479 (8) | 0.0541 (3) | |
| Br2 | 0.05033 (11) | 1.02044 (9) | 0.16420 (7) | 0.0468 (3) | |
| Br3 | 0.23105 (12) | 0.51574 (10) | 0.24364 (9) | 0.0574 (3) | |
| C1 | 0.6651 (12) | 0.3530 (9) | 0.1639 (8) | 0.050 (3) | |
| C2 | 0.8186 (12) | 0.3421 (10) | 0.0945 (8) | 0.054 (3) | |
| H2A | 0.8002 | 0.3855 | 0.0195 | 0.064* | |
| H2B | 0.8624 | 0.2589 | 0.1010 | 0.064* | |
| C3 | 0.3481 (11) | 1.1248 (8) | 0.3882 (8) | 0.046 (2) | |
| H3 | 0.3908 | 1.1706 | 0.3228 | 0.055* | |
| C4 | 0.3426 (13) | 1.1581 (10) | 0.4791 (10) | 0.063 (3) | |
| H4 | 0.3845 | 1.2235 | 0.4762 | 0.075* | |
| C5 | 0.2718 (12) | 1.0902 (10) | 0.5760 (8) | 0.053 (3) | |
| H5 | 0.2599 | 1.1127 | 0.6379 | 0.063* | |
| C6 | 0.2192 (11) | 0.9878 (9) | 0.5783 (7) | 0.044 (2) | |
| H6 | 0.1776 | 0.9388 | 0.6423 | 0.053* | |
| C7 | 0.2305 (9) | 0.9621 (8) | 0.4850 (7) | 0.032 (2) | |
| C8 | 0.1752 (10) | 0.8567 (8) | 0.4793 (6) | 0.037 (2) | |
| C9 | 0.1025 (11) | 0.7787 (8) | 0.5660 (7) | 0.044 (2) | |
| H9 | 0.0885 | 0.7895 | 0.6334 | 0.053* | |
| C10 | 0.0516 (13) | 0.6868 (10) | 0.5531 (8) | 0.060 (3) | |
| H10 | 0.0025 | 0.6345 | 0.6109 | 0.072* | |
| C11 | 0.0743 (13) | 0.6724 (10) | 0.4521 (8) | 0.060 (3) | |

| | | | | |
|---|---|---|---|---|
| H11 | 0.0404 | 0.6102 | 0.4408 | 0.072* |
| C12 | 0.1468 (13) | 0.7503 (9) | 0.3701 (8) | 0.056 (3) |
| H12 | 0.1618 | 0.7404 | 0.3022 | 0.067* |
| C13 | 0.3448 (12) | 1.1931 (8) | 0.1070 (8) | 0.051 (3) |
| H13 | 0.2437 | 1.2231 | 0.1343 | 0.061* |
| C14 | 0.4260 (13) | 1.2703 (9) | 0.0240 (8) | 0.053 (3) |
| H14 | 0.3792 | 1.3504 | −0.0047 | 0.063* |
| C15 | 0.5761 (12) | 1.2258 (9) | −0.0145 (7) | 0.046 (2) |
| H15 | 0.6328 | 1.2757 | −0.0695 | 0.055* |
| C16 | 0.6409 (11) | 1.1099 (9) | 0.0276 (7) | 0.047 (2) |
| H16 | 0.7429 | 1.0799 | 0.0014 | 0.056* |
| C17 | 0.5572 (10) | 1.0337 (8) | 0.1101 (6) | 0.034 (2) |
| C18 | 0.6133 (10) | 0.9048 (8) | 0.1607 (6) | 0.035 (2) |
| C19 | 0.7675 (11) | 0.8444 (9) | 0.1358 (8) | 0.049 (3) |
| H19 | 0.8377 | 0.8852 | 0.0837 | 0.059* |
| C20 | 0.8125 (13) | 0.7270 (10) | 0.1879 (9) | 0.060 (3) |
| H20 | 0.9151 | 0.6865 | 0.1735 | 0.072* |
| C21 | 0.7010 (13) | 0.6653 (9) | 0.2656 (9) | 0.059 (3) |
| H21 | 0.7287 | 0.5839 | 0.3015 | 0.071* |
| C22 | 0.5528 (12) | 0.7292 (9) | 0.2856 (8) | 0.053 (3) |
| H22 | 0.4799 | 0.6893 | 0.3359 | 0.063* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0381 (6) | 0.0378 (6) | 0.0242 (6) | −0.0070 (5) | 0.0117 (4) | −0.0077 (5) |
| N1 | 0.033 (4) | 0.043 (4) | 0.028 (4) | −0.007 (3) | 0.008 (3) | −0.016 (4) |
| N2 | 0.047 (5) | 0.040 (4) | 0.028 (4) | −0.016 (4) | 0.013 (3) | −0.007 (3) |
| N3 | 0.033 (4) | 0.036 (4) | 0.027 (4) | −0.004 (3) | 0.009 (3) | −0.002 (3) |
| N4 | 0.037 (4) | 0.033 (4) | 0.024 (4) | 0.000 (3) | 0.000 (3) | −0.007 (3) |
| O1 | 0.059 (5) | 0.053 (5) | 0.069 (5) | 0.006 (4) | 0.012 (4) | 0.007 (4) |
| O2 | 0.065 (6) | 0.085 (6) | 0.065 (5) | −0.006 (5) | 0.008 (4) | 0.034 (5) |
| O3 | 0.080 (10) | 0.041 (8) | 0.048 (8) | −0.015 (7) | −0.047 (8) | 0.007 (6) |
| Br1 | 0.0528 (7) | 0.0612 (7) | 0.0445 (6) | −0.0112 (5) | 0.0059 (5) | −0.0156 (5) |
| Br2 | 0.0376 (6) | 0.0617 (7) | 0.0353 (5) | −0.0075 (5) | 0.0033 (4) | −0.0117 (5) |
| Br3 | 0.0428 (6) | 0.0652 (7) | 0.0613 (7) | −0.0074 (5) | 0.0032 (5) | −0.0212 (6) |
| C1 | 0.049 (6) | 0.050 (6) | 0.046 (6) | −0.007 (5) | −0.007 (5) | −0.008 (5) |
| C2 | 0.049 (6) | 0.060 (7) | 0.044 (6) | −0.002 (5) | 0.005 (5) | −0.014 (5) |
| C3 | 0.052 (6) | 0.042 (6) | 0.042 (6) | −0.010 (5) | 0.006 (5) | −0.014 (5) |
| C4 | 0.063 (8) | 0.064 (7) | 0.083 (9) | −0.008 (6) | −0.024 (6) | −0.046 (7) |
| C5 | 0.057 (7) | 0.069 (7) | 0.036 (6) | 0.004 (6) | −0.012 (5) | −0.028 (6) |
| C6 | 0.044 (6) | 0.055 (6) | 0.023 (5) | 0.008 (5) | −0.002 (4) | −0.013 (5) |
| C7 | 0.021 (4) | 0.039 (5) | 0.029 (5) | 0.008 (4) | −0.006 (3) | −0.011 (4) |
| C8 | 0.031 (5) | 0.046 (6) | 0.021 (5) | −0.003 (4) | 0.008 (4) | 0.000 (4) |
| C9 | 0.042 (6) | 0.050 (6) | 0.025 (5) | −0.008 (5) | 0.004 (4) | 0.003 (4) |
| C10 | 0.064 (7) | 0.071 (8) | 0.037 (6) | −0.033 (6) | 0.012 (5) | 0.000 (5) |
| C11 | 0.077 (8) | 0.060 (7) | 0.043 (6) | −0.033 (6) | 0.014 (5) | −0.012 (5) |
| C12 | 0.077 (8) | 0.053 (7) | 0.037 (6) | −0.031 (6) | 0.009 (5) | −0.009 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C13 | 0.045 (6) | 0.043 (6) | 0.051 (6) | −0.002 (5) | 0.005 (5) | −0.007 (5) |
| C14 | 0.065 (7) | 0.035 (5) | 0.048 (6) | −0.012 (5) | −0.012 (5) | 0.004 (5) |
| C15 | 0.062 (7) | 0.048 (6) | 0.028 (5) | −0.021 (5) | 0.001 (4) | −0.006 (5) |
| C16 | 0.045 (6) | 0.062 (7) | 0.034 (5) | −0.023 (5) | 0.014 (4) | −0.016 (5) |
| C17 | 0.039 (5) | 0.043 (5) | 0.020 (4) | −0.012 (4) | −0.002 (4) | −0.010 (4) |
| C18 | 0.039 (5) | 0.047 (6) | 0.022 (4) | −0.007 (4) | −0.003 (4) | −0.014 (4) |
| C19 | 0.030 (5) | 0.062 (7) | 0.059 (7) | −0.004 (5) | 0.006 (4) | −0.031 (6) |
| C20 | 0.051 (7) | 0.061 (8) | 0.068 (7) | 0.010 (6) | −0.006 (6) | −0.033 (6) |
| C21 | 0.067 (8) | 0.043 (6) | 0.060 (7) | 0.012 (5) | −0.022 (6) | −0.014 (6) |
| C22 | 0.044 (6) | 0.060 (7) | 0.041 (6) | 0.003 (5) | −0.003 (5) | −0.007 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N3 | 1.985 (6) | C6—C7 | 1.355 (12) |
| Cu1—N2 | 1.997 (7) | C6—H6 | 0.9300 |
| Cu1—N4 | 2.078 (7) | C7—C8 | 1.489 (13) |
| Cu1—N1 | 2.125 (7) | C8—C9 | 1.388 (11) |
| Cu1—Br2 | 2.471 (2) | C9—C10 | 1.355 (14) |
| N1—C7 | 1.340 (10) | C9—H9 | 0.9300 |
| N1—C3 | 1.344 (11) | C10—C11 | 1.382 (14) |
| N2—C12 | 1.321 (12) | C10—H10 | 0.9300 |
| N2—C8 | 1.341 (11) | C11—C12 | 1.354 (13) |
| N3—C13 | 1.347 (11) | C11—H11 | 0.9300 |
| N3—C17 | 1.354 (10) | C12—H12 | 0.9300 |
| N4—C22 | 1.343 (12) | C13—C14 | 1.395 (13) |
| N4—C18 | 1.362 (10) | C13—H13 | 0.9300 |
| O1—C1 | 1.309 (12) | C14—C15 | 1.370 (14) |
| O1—H1 | 0.8200 | C14—H14 | 0.9300 |
| O2—C1 | 1.185 (11) | C15—C16 | 1.341 (14) |
| O3—H3A | 0.8500 | C15—H15 | 0.9300 |
| O3—H3B | 0.8500 | C16—C17 | 1.397 (12) |
| Br1—C2 | 1.972 (11) | C16—H16 | 0.9300 |
| C1—C2 | 1.496 (13) | C17—C18 | 1.472 (12) |
| C2—H2A | 0.9700 | C18—C19 | 1.408 (12) |
| C2—H2B | 0.9700 | C19—C20 | 1.347 (14) |
| C3—C4 | 1.381 (13) | C19—H19 | 0.9300 |
| C3—H3 | 0.9300 | C20—C21 | 1.431 (15) |
| C4—C5 | 1.406 (15) | C20—H20 | 0.9300 |
| C4—H4 | 0.9300 | C21—C22 | 1.368 (14) |
| C5—C6 | 1.406 (14) | C21—H21 | 0.9300 |
| C5—H5 | 0.9300 | C22—H22 | 0.9300 |
| N3—Cu1—N2 | 175.6 (3) | C6—C7—C8 | 122.2 (8) |
| N3—Cu1—N4 | 80.1 (3) | N2—C8—C9 | 119.5 (9) |
| N2—Cu1—N4 | 97.1 (3) | N2—C8—C7 | 116.3 (7) |
| N3—Cu1—N1 | 98.2 (3) | C9—C8—C7 | 124.2 (8) |
| N2—Cu1—N1 | 79.9 (3) | C10—C9—C8 | 120.4 (9) |
| N4—Cu1—N1 | 114.5 (3) | C10—C9—H9 | 119.8 |
| N3—Cu1—Br2 | 93.4 (2) | C8—C9—H9 | 119.8 |
| N2—Cu1—Br2 | 91.0 (2) | C9—C10—C11 | 118.7 (10) |

| | | | |
|---|---|---|---|
| N4—Cu1—Br2 | 127.57 (19) | C9—C10—H10 | 120.7 |
| N1—Cu1—Br2 | 117.90 (19) | C11—C10—H10 | 120.7 |
| C7—N1—C3 | 119.6 (8) | C12—C11—C10 | 118.8 (10) |
| C7—N1—Cu1 | 112.7 (5) | C12—C11—H11 | 120.6 |
| C3—N1—Cu1 | 127.7 (6) | C10—C11—H11 | 120.6 |
| C12—N2—C8 | 120.0 (8) | N2—C12—C11 | 122.6 (10) |
| C12—N2—Cu1 | 123.8 (6) | N2—C12—H12 | 118.7 |
| C8—N2—Cu1 | 116.2 (6) | C11—C12—H12 | 118.7 |
| C13—N3—C17 | 118.7 (7) | N3—C13—C14 | 121.9 (9) |
| C13—N3—Cu1 | 123.9 (6) | N3—C13—H13 | 119.0 |
| C17—N3—Cu1 | 117.4 (5) | C14—C13—H13 | 119.0 |
| C22—N4—C18 | 118.6 (8) | C15—C14—C13 | 118.7 (9) |
| C22—N4—Cu1 | 128.6 (6) | C15—C14—H14 | 120.7 |
| C18—N4—Cu1 | 112.8 (6) | C13—C14—H14 | 120.7 |
| C1—O1—H1 | 109.5 | C16—C15—C14 | 119.7 (9) |
| H3A—O3—H3B | 109.7 | C16—C15—H15 | 120.2 |
| O2—C1—O1 | 125.6 (10) | C14—C15—H15 | 120.2 |
| O2—C1—C2 | 122.2 (10) | C15—C16—C17 | 120.8 (9) |
| O1—C1—C2 | 112.1 (9) | C15—C16—H16 | 119.6 |
| C1—C2—Br1 | 106.9 (7) | C17—C16—H16 | 119.6 |
| C1—C2—H2A | 110.3 | N3—C17—C16 | 120.2 (8) |
| Br1—C2—H2A | 110.3 | N3—C17—C18 | 113.9 (7) |
| C1—C2—H2B | 110.3 | C16—C17—C18 | 126.0 (8) |
| Br1—C2—H2B | 110.3 | N4—C18—C19 | 121.4 (8) |
| H2A—C2—H2B | 108.6 | N4—C18—C17 | 115.8 (7) |
| N1—C3—C4 | 122.0 (9) | C19—C18—C17 | 122.7 (8) |
| N1—C3—H3 | 119.0 | C20—C19—C18 | 119.4 (10) |
| C4—C3—H3 | 119.0 | C20—C19—H19 | 120.3 |
| C3—C4—C5 | 117.9 (10) | C18—C19—H19 | 120.3 |
| C3—C4—H4 | 121.0 | C19—C20—C21 | 119.3 (10) |
| C5—C4—H4 | 121.0 | C19—C20—H20 | 120.3 |
| C4—C5—C6 | 119.1 (9) | C21—C20—H20 | 120.3 |
| C4—C5—H5 | 120.5 | C22—C21—C20 | 118.3 (10) |
| C6—C5—H5 | 120.5 | C22—C21—H21 | 120.9 |
| C7—C6—C5 | 118.5 (9) | C20—C21—H21 | 120.9 |
| C7—C6—H6 | 120.8 | N4—C22—C21 | 123.0 (10) |
| C5—C6—H6 | 120.8 | N4—C22—H22 | 118.5 |
| N1—C7—C6 | 122.8 (8) | C21—C22—H22 | 118.5 |
| N1—C7—C8 | 114.9 (7) | | |

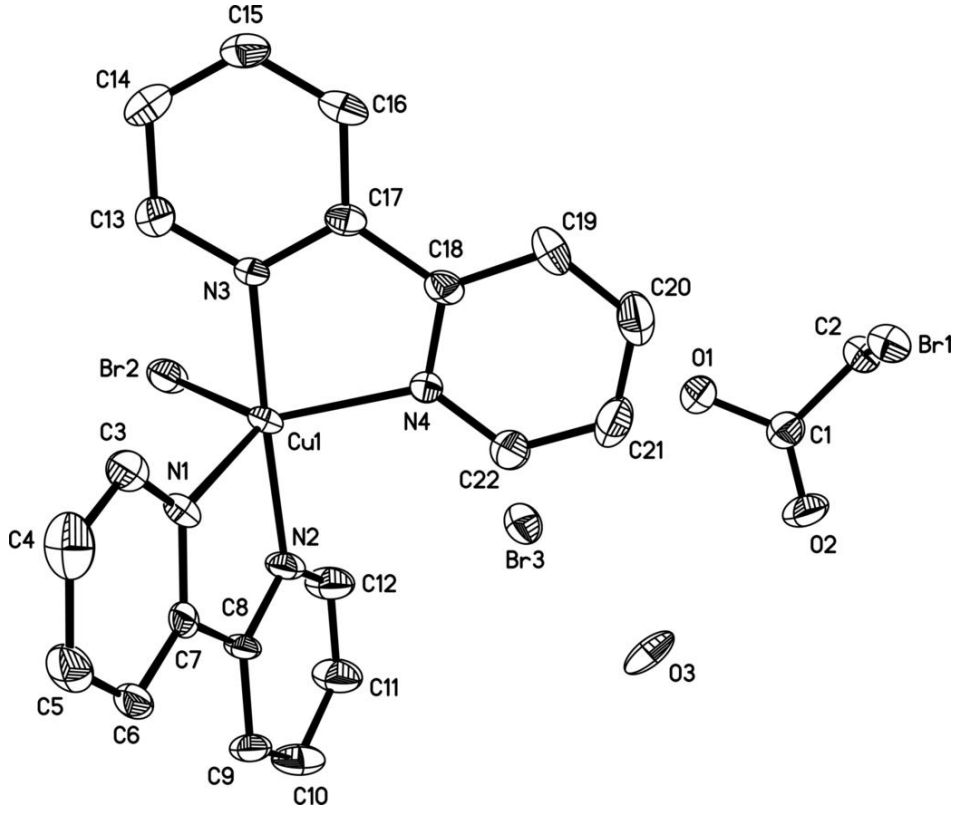
*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···Br3 | 0.82 | 2.34 | 3.129 (7) | 163 |
| O3—H3A···Br3 | 0.85 | 2.64 | 3.426 (11) | 154 |
| C14—H14···O1$^{i}$ | 0.93 | 2.46 | 3.254 (12) | 144 |
| C16—H16···Br2$^{i}$ | 0.93 | 3.01 | 3.835 (9) | 149 |
| C3—H3···O2$^{ii}$ | 0.93 | 2.60 | 3.374 (12) | 141 |

| | | | | |
|---|---|---|---|---|
| C4—H4···O3$^{ii}$ | 0.93 | 2.65 | 3.578 (16) | 172 |
| C10—H10···Br1$^{iii}$ | 0.93 | 3.13 | 3.751 (10) | 126 |
| C2—H2B···Br2$^{iv}$ | 0.97 | 2.88 | 3.815 (11) | 163 |
| C13—H13···Br1$^{v}$ | 0.93 | 2.89 | 3.750 (10) | 154 |

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*+1, *y*−1, *z*; (v) *x*−1, *y*+1, *z*.

**Fig. 1**


C15
C14
C16
C13
C17
C19
C18
N3
C20
C2
Br1
O1
Br2
N4
C1
C3
Cu1
C21
N1
C22
C4
N2
Br3
O2
C12
C8
C7
O3
C11
C5
C6
C9
C10