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# Bis[bis(1*H*-pyrazol-1-yl)methane-$\kappa^2N^2,N^{2'}$](formato-$\kappa^2O,O'$)copper(II) perchlorate

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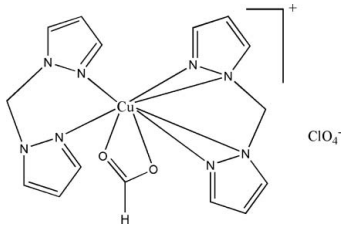
Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.008 Å; disorder in solvent or counterion; $R$ factor = 0.052; $wR$ factor = 0.165; data-to-parameter ratio = 10.8.

In the crystal structure of the title compound, $[Cu(HCO_2)(C_7H_8N_4)_2]ClO_4$, the $Cu^{II}$ ion is octahedrally coordinated by one bidentate formate ion and two bidentate bis(1*H*-pyrazol-1-yl)methane ligands. There are C—H···O hydrogen bonds and $\pi$–$\pi$ interactions [centroid–centroid distance = 3.487 (3) Å] in the crystal structure. The perchlorate anion is disordered over two positions with an occupancy ratio of 0.628 (9):0.372 (9).

## Related literature

For applications of coordination polymers, see: Kitagawa *et al.* (2004); Robson (2000). For synthesis of the bis(pyrazol-1-yl)methane ligand, see: Elguero *et al.* (1982).




## Experimental

### Crystal data

$[Cu(CHO_2)(C_7H_8N_4)_2]ClO_4$
$M_r$ = 504.36
Monoclinic, $P2_1/n$
$a$ = 11.0458 (19) Å
$b$ = 14.816 (3) Å
$c$ = 12.273 (2) Å
$\beta$ = 99.031 (3)°
$V$ = 1983.6 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.29 mm$^{-1}$
$T$ = 294 K
0.22 × 0.20 × 0.16 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.768, $T_{max}$ = 1.000
9920 measured reflections
3439 independent reflections
2334 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.165
$S$ = 1.02
3439 reflections
318 parameters
122 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.07 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.62 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C13—H13···O2$^{i}$ | 0.93 | 2.66 | 3.424 (7) | 140 |
| C4—H4$B$···O4$^{ii}$ | 0.97 | 2.37 | 3.343 (14) | 176 |
| C4—H4$B$···O4$'^{ii}$ | 0.97 | 2.66 | 3.580 (12) | 159 |
| C11—H11$B$···O5$^{iii}$ | 0.97 | 2.60 | 3.525 (17) | 161 |
| C11—H11$B$···O5$'^{iii}$ | 0.97 | 2.32 | 3.286 (9) | 176 |
| C12—H12···O3$^{iii}$ | 0.93 | 2.49 | 3.220 (14) | 136 |
| C12—H12···O3$'^{iii}$ | 0.93 | 2.30 | 3.195 (10) | 161 |

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

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1998); data reduction: *SAINT-NT*; 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: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2326).

## References

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Robson, R. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3735–3744.
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# supporting information

*Acta Cryst.* (2011). E**67**, m1486 [doi:10.1107/S1600536811039675]

# Bis[bis(1*H*-pyrazol-1-yl)methane-$\kappa^2N^2,N^{2'}$](formato-$\kappa^2O,O'$)copper(II) perchlorate

**Cai-Juan Zhao and Rui-Feng Zhang**

## S1. Comment

Coordination polymers have received significant attention in recent years, primarily due to their potential applications in many areas such as catalysis, molecular adsorption, magnetism properties and non-linear optics (Kitagawa *et al.*, 2004; Robson, 2000). We report herein the structure of the title compound, namely $[Cu(L_1)_2(HCO_2)]ClO_4$ ($L_1$ = bis(pyrazol-1-yl)methane). The title compound crystallizes in monoclinic space group $P2_1/n$. The asymmetrical unit of the unit cell contains one $Cu^{II}$ ion, one formic acid and two ligand $L_1$ (as shown in Fig. 1). The Cu ion is octahedrally coordinated to two oxygen atoms from one formate ion and four nitrogen atoms from two $L_1$ ligands. In the crystal structure, intermolecular C—H···O hydrogen bonds link the molecules into a three-dimensional network (Fig. 2), and $\pi$-$\pi$ interactions between two pyrazole rings (centroid-centroid distance is 3.487 Å) consolidate the crystal packing.

## S2. Experimental

The ligand $L_1$ was synthesized according to literature (Elguero *et al.*, 1982). The title compound was prepared by adding 5 ml methanol solution of copper(II) perchlorate (0.3 mmol) to 10 ml aqueous solution of $L_1$ (0.5 mmol) and formic acid (0.3 mmol). The mixture was stirred for half an hour and filtered. The filtrate was slowly evaporated at room temperature to yield blue cubic crystals suitable for X-ray analysis. Analysis calculated for $C_{15}H_{17}ClCuN_8$: C 35.69, H 3.37, N 22.21%; found: C 33.21, H 3.09, N 24.03%.

## S3. Refinement

Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms with C—H distances in the range of 0.93–0.97 Å, $U_{iso}(H) = 1.2U_{eq}(C)$.

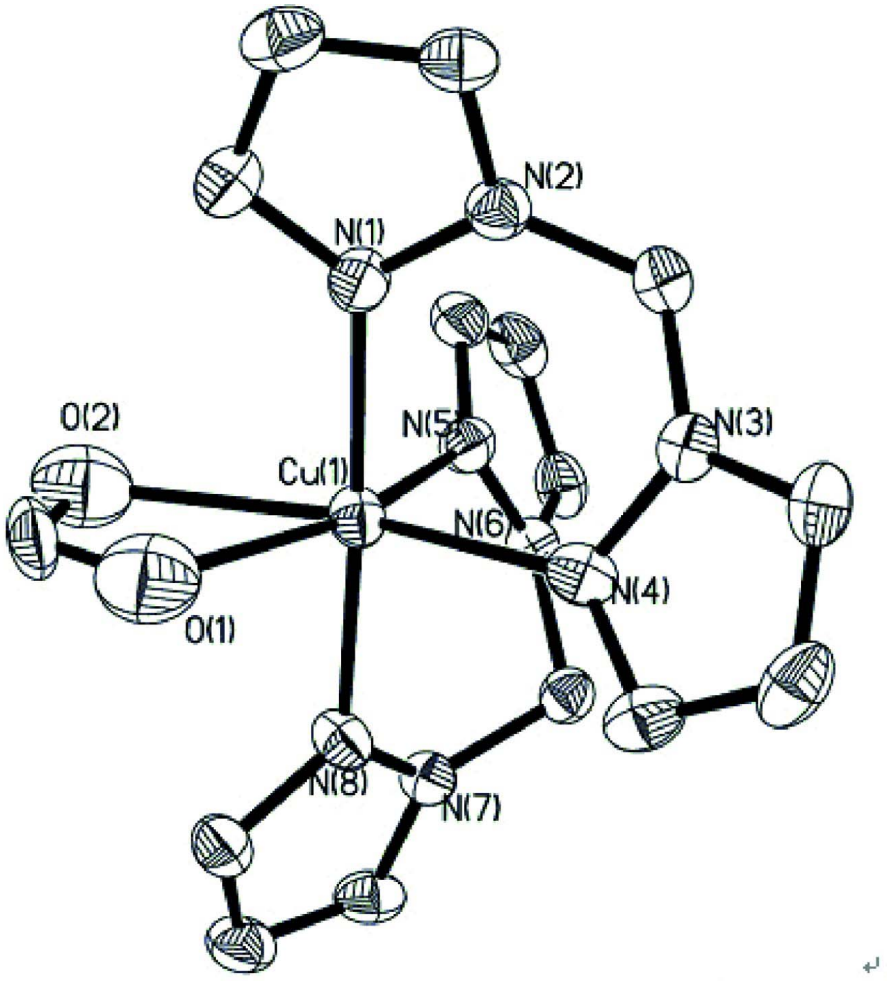


**Figure 1**

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. (Hydrogen atoms and the perchlorate ion are omitted for clarity.)

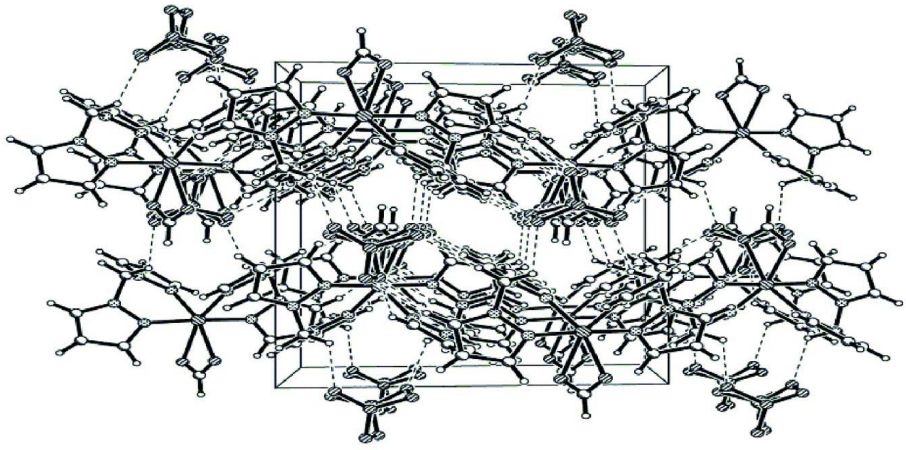

**Figure 2**

The packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

**Bis[bis(1*H*-pyrazol-1-yl)methane-$\kappa^2N^2,N^{2'}$](formato-$\kappa^2O,O'$)copper(II) perchlorate**

*Crystal data*

$[Cu(CHO_2)(C_7H_8N_4)_2]ClO_4$
$M_r$ = 504.36
Monoclinic, $P2_1/n$
$a$ = 11.0458 (19) Å
$b$ = 14.816 (3) Å
$c$ = 12.273 (2) Å
$\beta$ = 99.031 (3)°
$V$ = 1983.6 (6) Å$^3$
$Z$ = 4
$F(000)$ = 1028
$D_x$ = 1.689 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 3002 reflections
$\theta$ = 2.2–25.4°
$\mu$ = 1.29 mm$^{-1}$
$T$ = 294 K
Cubic, blue
0.22 × 0.20 × 0.16 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.768, $T_{max}$ = 1.000
9920 measured reflections
3439 independent reflections
2334 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.2°
$h$ = −8→13
$k$ = −17→16
$l$ = −14→14

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.165
$S$ = 1.02
3439 reflections
318 parameters
122 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.099P)^2 + 1.4485P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.07 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.62 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0099 (12)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.51417 (5) | 0.18886 (4) | 0.24183 (4) | 0.0406 (3) | |
| O1 | 0.4358 (5) | 0.0590 (4) | 0.1916 (4) | 0.0968 (16) | |
| O2 | 0.5977 (5) | 0.0465 (4) | 0.2919 (4) | 0.0984 (16) | |
| N1 | 0.6033 (4) | 0.1867 (3) | 0.1089 (3) | 0.0448 (9) | |
| N2 | 0.5865 (3) | 0.2511 (3) | 0.0313 (3) | 0.0431 (9) | |
| N3 | 0.4141 (3) | 0.3339 (2) | 0.0709 (3) | 0.0410 (9) | |
| N4 | 0.3848 (3) | 0.2847 (3) | 0.1554 (3) | 0.0451 (10) | |
| N5 | 0.6403 (3) | 0.2826 (3) | 0.3261 (3) | 0.0427 (9) | |
| N6 | 0.6134 (3) | 0.3316 (2) | 0.4117 (3) | 0.0388 (9) | |
| N7 | 0.4428 (3) | 0.2470 (2) | 0.4540 (3) | 0.0405 (9) | |
| N8 | 0.4262 (4) | 0.1837 (2) | 0.3739 (3) | 0.0457 (9) | |
| C1 | 0.6507 (5) | 0.1161 (3) | 0.0628 (4) | 0.0550 (13) | |
| H1 | 0.6716 | 0.0613 | 0.0978 | 0.066* | |
| C2 | 0.6644 (5) | 0.1366 (4) | −0.0450 (4) | 0.0559 (13) | |
| H2 | 0.6959 | 0.0993 | −0.0946 | 0.067* | |
| C3 | 0.6224 (4) | 0.2217 (4) | −0.0628 (4) | 0.0504 (12) | |
| H3 | 0.6188 | 0.2543 | −0.1281 | 0.060* | |
| C4 | 0.5405 (4) | 0.3388 (3) | 0.0552 (4) | 0.0435 (11) | |
| H4A | 0.5896 | 0.3628 | 0.1213 | 0.052* | |
| H4B | 0.5478 | 0.3796 | −0.0053 | 0.052* | |
| C5 | 0.3162 (5) | 0.3769 (3) | 0.0150 (4) | 0.0504 (12) | |
| H5 | 0.3156 | 0.4142 | −0.0460 | 0.061* | |
| C6 | 0.2190 (5) | 0.3555 (4) | 0.0647 (5) | 0.0593 (14) | |
| H6 | 0.1385 | 0.3750 | 0.0451 | 0.071* | |
| C7 | 0.2642 (4) | 0.2986 (4) | 0.1508 (4) | 0.0532 (13) | |
| H7 | 0.2170 | 0.2732 | 0.1993 | 0.064* | |
| C8 | 0.7606 (5) | 0.2959 (3) | 0.3287 (4) | 0.0518 (13) | |
| H8 | 0.8065 | 0.2702 | 0.2793 | 0.062* | |
| C9 | 0.8077 (5) | 0.3525 (4) | 0.4143 (5) | 0.0570 (13) | |
| H9 | 0.8884 | 0.3718 | 0.4326 | 0.068* | |
| C10 | 0.7118 (4) | 0.3739 (3) | 0.4658 (4) | 0.0496 (12) | |
| H10 | 0.7140 | 0.4109 | 0.5272 | 0.059* | |
| C11 | 0.4874 (4) | 0.3361 (3) | 0.4292 (4) | 0.0417 (10) | |
| H11A | 0.4371 | 0.3598 | 0.3635 | 0.050* | |
| H11B | 0.4808 | 0.3767 | 0.4899 | 0.050* | |
| C12 | 0.4066 (4) | 0.2174 (4) | 0.5466 (4) | 0.0522 (13) | |
| H12 | 0.4091 | 0.2498 | 0.6118 | 0.063* | |
| C13 | 0.3656 (5) | 0.1318 (4) | 0.5284 (4) | 0.0574 (14) | |
| H13 | 0.3350 | 0.0940 | 0.5781 | 0.069* | |
| C14 | 0.3787 (5) | 0.1122 (3) | 0.4204 (4) | 0.0513 (12) | |
| H14 | 0.3577 | 0.0576 | 0.3851 | 0.062* | |
| C15 | 0.5126 (7) | 0.0079 (4) | 0.2389 (5) | 0.0663 (18) | |
| H15 | 0.5063 | −0.0547 | 0.2345 | 0.080* | |
| Cl1 | 0.48695 (14) | 0.56011 (9) | 0.25933 (10) | 0.0592 (4) | |
| O3 | 0.4395 (14) | 0.6517 (6) | 0.2731 (10) | 0.094 (5) | 0.372 (9) |

| | | | | | |
|---|---|---|---|---|---|
| O4 | 0.4250 (15) | 0.5272 (9) | 0.1570 (8) | 0.110 (6) | 0.372 (9) |
| O5 | 0.4583 (17) | 0.5091 (9) | 0.3505 (10) | 0.145 (7) | 0.372 (9) |
| O6 | 0.6157 (8) | 0.5647 (14) | 0.2589 (18) | 0.267 (14) | 0.372 (9) |
| O3′ | 0.5275 (10) | 0.6523 (5) | 0.2451 (7) | 0.125 (4) | 0.628 (9) |
| O4′ | 0.5199 (12) | 0.5081 (7) | 0.1726 (8) | 0.147 (4) | 0.628 (9) |
| O5′ | 0.5488 (9) | 0.5305 (5) | 0.3645 (5) | 0.094 (3) | 0.628 (9) |
| O6′ | 0.3574 (7) | 0.5562 (10) | 0.2584 (13) | 0.259 (9) | 0.628 (9) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0503 (4) | 0.0379 (4) | 0.0332 (4) | −0.0003 (2) | 0.0051 (2) | 0.0002 (2) |
| O1 | 0.109 (4) | 0.118 (4) | 0.067 (3) | −0.004 (3) | 0.023 (3) | −0.008 (3) |
| O2 | 0.108 (4) | 0.127 (5) | 0.063 (3) | −0.003 (3) | 0.021 (3) | 0.007 (3) |
| N1 | 0.053 (2) | 0.044 (2) | 0.037 (2) | 0.0068 (18) | 0.0069 (18) | 0.0010 (18) |
| N2 | 0.044 (2) | 0.048 (2) | 0.038 (2) | 0.0015 (17) | 0.0081 (17) | 0.0010 (18) |
| N3 | 0.042 (2) | 0.039 (2) | 0.040 (2) | 0.0013 (16) | 0.0004 (17) | −0.0036 (17) |
| N4 | 0.044 (2) | 0.055 (2) | 0.036 (2) | −0.0080 (18) | 0.0048 (18) | 0.0002 (18) |
| N5 | 0.044 (2) | 0.046 (2) | 0.038 (2) | 0.0073 (17) | 0.0067 (17) | 0.0045 (17) |
| N6 | 0.041 (2) | 0.039 (2) | 0.0358 (19) | −0.0028 (16) | 0.0023 (17) | −0.0004 (16) |
| N7 | 0.041 (2) | 0.042 (2) | 0.040 (2) | −0.0030 (16) | 0.0080 (17) | −0.0003 (17) |
| N8 | 0.052 (2) | 0.041 (2) | 0.044 (2) | −0.0103 (18) | 0.0100 (18) | 0.0011 (18) |
| C1 | 0.057 (3) | 0.050 (3) | 0.060 (3) | 0.008 (2) | 0.014 (3) | −0.005 (2) |
| C2 | 0.052 (3) | 0.066 (4) | 0.052 (3) | −0.004 (3) | 0.016 (2) | −0.016 (3) |
| C3 | 0.051 (3) | 0.064 (3) | 0.038 (2) | −0.002 (2) | 0.011 (2) | −0.002 (2) |
| C4 | 0.047 (3) | 0.040 (3) | 0.043 (2) | −0.001 (2) | 0.004 (2) | 0.005 (2) |
| C5 | 0.056 (3) | 0.042 (3) | 0.049 (3) | 0.006 (2) | −0.006 (2) | −0.003 (2) |
| C6 | 0.040 (3) | 0.057 (3) | 0.075 (4) | 0.011 (2) | −0.008 (3) | −0.016 (3) |
| C7 | 0.041 (3) | 0.064 (3) | 0.056 (3) | −0.003 (2) | 0.009 (2) | −0.015 (3) |
| C8 | 0.048 (3) | 0.055 (3) | 0.055 (3) | 0.005 (2) | 0.014 (2) | 0.016 (2) |
| C9 | 0.043 (3) | 0.057 (3) | 0.068 (3) | −0.009 (2) | −0.003 (3) | 0.018 (3) |
| C10 | 0.051 (3) | 0.039 (3) | 0.055 (3) | −0.008 (2) | −0.005 (2) | 0.003 (2) |
| C11 | 0.042 (2) | 0.040 (3) | 0.043 (2) | 0.0008 (19) | 0.007 (2) | −0.004 (2) |
| C12 | 0.045 (3) | 0.074 (4) | 0.039 (3) | 0.001 (2) | 0.012 (2) | 0.004 (2) |
| C13 | 0.054 (3) | 0.070 (4) | 0.052 (3) | 0.002 (3) | 0.017 (3) | 0.018 (3) |
| C14 | 0.056 (3) | 0.043 (3) | 0.057 (3) | −0.007 (2) | 0.015 (2) | 0.002 (2) |
| C15 | 0.111 (6) | 0.027 (3) | 0.067 (4) | −0.004 (3) | 0.032 (4) | −0.001 (3) |
| Cl1 | 0.0867 (10) | 0.0433 (8) | 0.0434 (7) | 0.0043 (6) | −0.0028 (7) | −0.0003 (5) |
| O3 | 0.114 (9) | 0.069 (7) | 0.095 (8) | 0.029 (6) | 0.004 (7) | −0.013 (6) |
| O4 | 0.136 (10) | 0.099 (8) | 0.087 (8) | −0.010 (7) | −0.006 (7) | −0.005 (7) |
| O5 | 0.145 (7) | 0.145 (7) | 0.144 (7) | −0.0001 (11) | 0.0230 (16) | 0.0005 (11) |
| O6 | 0.267 (14) | 0.267 (14) | 0.267 (14) | 0.0001 (11) | 0.042 (2) | 0.0000 (11) |
| O3′ | 0.156 (8) | 0.089 (6) | 0.121 (7) | −0.025 (5) | −0.004 (6) | 0.010 (5) |
| O4′ | 0.167 (8) | 0.148 (8) | 0.137 (7) | −0.020 (6) | 0.057 (6) | −0.036 (6) |
| O5′ | 0.130 (6) | 0.074 (5) | 0.070 (4) | −0.004 (4) | −0.011 (4) | 0.026 (4) |
| O6′ | 0.216 (11) | 0.289 (13) | 0.272 (13) | 0.000 (9) | 0.038 (9) | −0.026 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—N8 | 2.018 (4) | C4—H4A | 0.9700 |
| Cu1—N1 | 2.034 (4) | C4—H4B | 0.9700 |
| Cu1—N5 | 2.119 (4) | C5—C6 | 1.353 (7) |
| Cu1—O1 | 2.160 (5) | C5—H5 | 0.9300 |
| Cu1—N4 | 2.169 (4) | C6—C7 | 1.383 (8) |
| Cu1—O2 | 2.345 (6) | C6—H6 | 0.9300 |
| O1—C15 | 1.215 (7) | C7—H7 | 0.9300 |
| O2—C15 | 1.201 (7) | C8—C9 | 1.380 (8) |
| N1—C1 | 1.334 (6) | C8—H8 | 0.9300 |
| N1—N2 | 1.340 (5) | C9—C10 | 1.354 (8) |
| N2—C3 | 1.350 (6) | C9—H9 | 0.9300 |
| N2—C4 | 1.443 (6) | C10—H10 | 0.9300 |
| N3—C5 | 1.346 (6) | C11—H11A | 0.9700 |
| N3—N4 | 1.347 (5) | C11—H11B | 0.9700 |
| N3—C4 | 1.441 (6) | C12—C13 | 1.353 (8) |
| N4—C7 | 1.340 (6) | C12—H12 | 0.9300 |
| N5—C8 | 1.339 (6) | C13—C14 | 1.388 (7) |
| N5—N6 | 1.347 (5) | C13—H13 | 0.9300 |
| N6—C10 | 1.338 (6) | C14—H14 | 0.9300 |
| N6—C11 | 1.442 (6) | C15—H15 | 0.9300 |
| N7—C12 | 1.338 (6) | Cl1—O4′ | 1.408 (6) |
| N7—N8 | 1.350 (5) | Cl1—O4 | 1.419 (7) |
| N7—C11 | 1.458 (6) | Cl1—O6 | 1.425 (8) |
| N8—C14 | 1.347 (6) | Cl1—O5 | 1.427 (8) |
| C1—C2 | 1.388 (7) | Cl1—O6′ | 1.431 (7) |
| C1—H1 | 0.9300 | Cl1—O5′ | 1.432 (5) |
| C2—C3 | 1.351 (7) | Cl1—O3′ | 1.456 (6) |
| C2—H2 | 0.9300 | Cl1—O3 | 1.473 (7) |
| C3—H3 | 0.9300 | | |
| | | | |
| N8—Cu1—N1 | 176.90 (16) | C5—C6—H6 | 127.2 |
| N8—Cu1—N5 | 89.75 (15) | C7—C6—H6 | 127.2 |
| N1—Cu1—N5 | 92.19 (15) | N4—C7—C6 | 111.3 (5) |
| N8—Cu1—O1 | 88.46 (16) | N4—C7—H7 | 124.4 |
| N1—Cu1—O1 | 88.83 (17) | C6—C7—H7 | 124.4 |
| N5—Cu1—O1 | 157.97 (19) | N5—C8—C9 | 111.2 (5) |
| N8—Cu1—N4 | 93.12 (15) | N5—C8—H8 | 124.4 |
| N1—Cu1—N4 | 89.00 (15) | C9—C8—H8 | 124.4 |
| N5—Cu1—N4 | 98.13 (16) | C10—C9—C8 | 105.6 (4) |
| O1—Cu1—N4 | 103.89 (19) | C10—C9—H9 | 127.2 |
| N8—Cu1—O2 | 88.52 (16) | C8—C9—H9 | 127.2 |
| N1—Cu1—O2 | 88.64 (16) | N6—C10—C9 | 107.0 (5) |
| N5—Cu1—O2 | 105.09 (18) | N6—C10—H10 | 126.5 |
| O1—Cu1—O2 | 52.9 (2) | C9—C10—H10 | 126.5 |
| N4—Cu1—O2 | 156.73 (18) | N6—C11—N7 | 110.8 (3) |
| C15—O1—Cu1 | 101.5 (4) | N6—C11—H11A | 109.5 |

| | | | |
|---|---|---|---|
| C15—O2—Cu1 | 92.5 (4) | N7—C11—H11A | 109.5 |
| C1—N1—N2 | 106.0 (4) | N6—C11—H11B | 109.5 |
| C1—N1—Cu1 | 128.6 (3) | N7—C11—H11B | 109.5 |
| N2—N1—Cu1 | 121.9 (3) | H11A—C11—H11B | 108.1 |
| N1—N2—C3 | 110.7 (4) | N7—C12—C13 | 107.7 (4) |
| N1—N2—C4 | 120.7 (4) | N7—C12—H12 | 126.2 |
| C3—N2—C4 | 128.6 (4) | C13—C12—H12 | 126.2 |
| C5—N3—N4 | 112.2 (4) | C12—C13—C14 | 105.7 (4) |
| C5—N3—C4 | 128.7 (4) | C12—C13—H13 | 127.1 |
| N4—N3—C4 | 119.0 (4) | C14—C13—H13 | 127.1 |
| C7—N4—N3 | 104.0 (4) | N8—C14—C13 | 110.3 (5) |
| C7—N4—Cu1 | 134.0 (3) | N8—C14—H14 | 124.9 |
| N3—N4—Cu1 | 120.7 (3) | C13—C14—H14 | 124.9 |
| C8—N5—N6 | 104.0 (4) | O2—C15—O1 | 113.0 (6) |
| C8—N5—Cu1 | 133.0 (3) | O2—C15—H15 | 123.5 |
| N6—N5—Cu1 | 121.7 (3) | O1—C15—H15 | 123.5 |
| C10—N6—N5 | 112.2 (4) | O4′—Cl1—O4 | 44.7 (6) |
| C10—N6—C11 | 129.2 (4) | O4′—Cl1—O6 | 69.3 (8) |
| N5—N6—C11 | 118.5 (4) | O4—Cl1—O6 | 110.9 (7) |
| C12—N7—N8 | 111.5 (4) | O4′—Cl1—O5 | 114.8 (9) |
| C12—N7—C11 | 129.0 (4) | O4—Cl1—O5 | 112.1 (7) |
| N8—N7—C11 | 119.3 (3) | O6—Cl1—O5 | 111.9 (7) |
| C14—N8—N7 | 104.8 (4) | O4′—Cl1—O6′ | 110.4 (6) |
| C14—N8—Cu1 | 129.7 (3) | O4—Cl1—O6′ | 68.7 (7) |
| N7—N8—Cu1 | 122.0 (3) | O6—Cl1—O6′ | 179.2 (9) |
| N1—C1—C2 | 109.9 (5) | O5—Cl1—O6′ | 68.9 (8) |
| N1—C1—H1 | 125.0 | O4′—Cl1—O5′ | 111.8 (6) |
| C2—C1—H1 | 125.0 | O4—Cl1—O5′ | 142.0 (7) |
| C3—C2—C1 | 105.8 (4) | O6—Cl1—O5′ | 71.5 (8) |
| C3—C2—H2 | 127.1 | O5—Cl1—O5′ | 42.6 (7) |
| C1—C2—H2 | 127.1 | O6′—Cl1—O5′ | 109.3 (6) |
| N2—C3—C2 | 107.5 (4) | O4′—Cl1—O3′ | 107.6 (5) |
| N2—C3—H3 | 126.2 | O4—Cl1—O3′ | 109.3 (7) |
| C2—C3—H3 | 126.2 | O6—Cl1—O3′ | 68.2 (9) |
| N3—C4—N2 | 111.2 (4) | O5—Cl1—O3′ | 134.5 (8) |
| N3—C4—H4A | 109.4 | O6′—Cl1—O3′ | 111.3 (6) |
| N2—C4—H4A | 109.4 | O5′—Cl1—O3′ | 106.4 (4) |
| N3—C4—H4B | 109.4 | O4′—Cl1—O3 | 136.9 (7) |
| N2—C4—H4B | 109.4 | O4—Cl1—O3 | 106.7 (6) |
| H4A—C4—H4B | 108.0 | O6—Cl1—O3 | 109.2 (7) |
| N3—C5—C6 | 106.9 (5) | O5—Cl1—O3 | 105.7 (6) |
| N3—C5—H5 | 126.6 | O6′—Cl1—O3 | 70.4 (8) |
| C6—C5—H5 | 126.6 | O5′—Cl1—O3 | 107.8 (6) |
| C5—C6—C7 | 105.7 (4) | O3′—Cl1—O3 | 43.3 (7) |
| | | | |
| N8—Cu1—O1—C15 | −89.2 (4) | C8—N5—N6—C11 | 176.7 (4) |
| N1—Cu1—O1—C15 | 89.3 (4) | Cu1—N5—N6—C11 | −14.9 (5) |
| N5—Cu1—O1—C15 | −3.7 (7) | C12—N7—N8—C14 | −0.6 (5) |

| | | | |
|---|---|---|---|
| N4—Cu1—O1—C15 | 178.0 (4) | C11—N7—N8—C14 | −176.6 (4) |
| O2—Cu1—O1—C15 | 0.1 (3) | C12—N7—N8—Cu1 | −161.4 (3) |
| N8—Cu1—O2—C15 | 89.1 (4) | C11—N7—N8—Cu1 | 22.6 (5) |
| N1—Cu1—O2—C15 | −89.7 (4) | N1—Cu1—N8—C14 | −10 (3) |
| N5—Cu1—O2—C15 | 178.4 (3) | N5—Cu1—N8—C14 | −139.0 (5) |
| O1—Cu1—O2—C15 | −0.1 (3) | O1—Cu1—N8—C14 | 19.0 (5) |
| N4—Cu1—O2—C15 | −5.4 (6) | N4—Cu1—N8—C14 | 122.8 (4) |
| N8—Cu1—N1—C1 | −6 (3) | O2—Cu1—N8—C14 | −33.9 (5) |
| N5—Cu1—N1—C1 | 123.0 (4) | N1—Cu1—N8—N7 | 145 (3) |
| O1—Cu1—N1—C1 | −35.0 (5) | N5—Cu1—N8—N7 | 16.5 (4) |
| N4—Cu1—N1—C1 | −138.9 (4) | O1—Cu1—N8—N7 | 174.6 (4) |
| O2—Cu1—N1—C1 | 17.9 (5) | N4—Cu1—N8—N7 | −81.6 (4) |
| N8—Cu1—N1—N2 | 150 (3) | O2—Cu1—N8—N7 | 121.6 (4) |
| N5—Cu1—N1—N2 | −81.0 (3) | N2—N1—C1—C2 | 0.2 (6) |
| O1—Cu1—N1—N2 | 121.0 (4) | Cu1—N1—C1—C2 | 159.2 (4) |
| N4—Cu1—N1—N2 | 17.1 (3) | N1—C1—C2—C3 | −0.6 (6) |
| O2—Cu1—N1—N2 | 174.0 (4) | N1—N2—C3—C2 | −0.6 (5) |
| C1—N1—N2—C3 | 0.2 (5) | C4—N2—C3—C2 | 176.9 (4) |
| Cu1—N1—N2—C3 | −160.5 (3) | C1—C2—C3—N2 | 0.7 (6) |
| C1—N1—N2—C4 | −177.5 (4) | C5—N3—C4—N2 | −121.3 (5) |
| Cu1—N1—N2—C4 | 21.8 (5) | N4—N3—C4—N2 | 62.9 (5) |
| C5—N3—N4—C7 | −0.1 (5) | N1—N2—C4—N3 | −69.0 (5) |
| C4—N3—N4—C7 | 176.3 (4) | C3—N2—C4—N3 | 113.8 (5) |
| C5—N3—N4—Cu1 | 168.7 (3) | N4—N3—C5—C6 | 0.2 (5) |
| C4—N3—N4—Cu1 | −14.9 (5) | C4—N3—C5—C6 | −175.9 (4) |
| N8—Cu1—N4—C7 | −33.5 (4) | N3—C5—C6—C7 | −0.1 (6) |
| N1—Cu1—N4—C7 | 144.3 (4) | N3—N4—C7—C6 | 0.0 (5) |
| N5—Cu1—N4—C7 | −123.7 (4) | Cu1—N4—C7—C6 | −166.6 (4) |
| O1—Cu1—N4—C7 | 55.7 (5) | C5—C6—C7—N4 | 0.1 (6) |
| O2—Cu1—N4—C7 | 60.1 (6) | N6—N5—C8—C9 | −0.3 (5) |
| N8—Cu1—N4—N3 | 161.7 (3) | Cu1—N5—C8—C9 | −166.8 (3) |
| N1—Cu1—N4—N3 | −20.6 (3) | N5—C8—C9—C10 | 0.4 (6) |
| N5—Cu1—N4—N3 | 71.5 (3) | N5—N6—C10—C9 | 0.1 (5) |
| O1—Cu1—N4—N3 | −109.1 (3) | C11—N6—C10—C9 | −176.0 (4) |
| O2—Cu1—N4—N3 | −104.8 (4) | C8—C9—C10—N6 | −0.3 (5) |
| N8—Cu1—N5—C8 | 143.9 (4) | C10—N6—C11—N7 | −120.8 (5) |
| N1—Cu1—N5—C8 | −33.7 (4) | N5—N6—C11—N7 | 63.2 (5) |
| O1—Cu1—N5—C8 | 58.6 (6) | C12—N7—C11—N6 | 115.5 (5) |
| N4—Cu1—N5—C8 | −123.0 (4) | N8—N7—C11—N6 | −69.2 (5) |
| O2—Cu1—N5—C8 | 55.5 (4) | N8—N7—C12—C13 | 0.5 (6) |
| N8—Cu1—N5—N6 | −20.7 (3) | C11—N7—C12—C13 | 176.1 (4) |
| N1—Cu1—N5—N6 | 161.7 (3) | N7—C12—C13—C14 | −0.3 (6) |
| O1—Cu1—N5—N6 | −106.0 (5) | N7—N8—C14—C13 | 0.4 (6) |
| N4—Cu1—N5—N6 | 72.4 (3) | Cu1—N8—C14—C13 | 159.1 (4) |
| O2—Cu1—N5—N6 | −109.1 (3) | C12—C13—C14—N8 | 0.0 (6) |
| C8—N5—N6—C10 | 0.1 (5) | Cu1—O2—C15—O1 | 0.2 (5) |
| Cu1—N5—N6—C10 | 168.5 (3) | Cu1—O1—C15—O2 | −0.2 (6) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C13—H13···O2$^{i}$ | 0.93 | 2.66 | 3.424 (7) | 140 |
| C4—H4*B*···O4$^{ii}$ | 0.97 | 2.37 | 3.343 (14) | 176 |
| C4—H4*B*···O4′$^{ii}$ | 0.97 | 2.66 | 3.580 (12) | 159 |
| C11—H11*B*···O5$^{iii}$ | 0.97 | 2.60 | 3.525 (17) | 161 |
| C11—H11*B*···O5′$^{iii}$ | 0.97 | 2.32 | 3.286 (9) | 176 |
| C12—H12···O3$^{iii}$ | 0.93 | 2.49 | 3.220 (14) | 136 |
| C12—H12···O3′$^{iii}$ | 0.93 | 2.30 | 3.195 (10) | 161 |

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