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# The cocrystal $\mu$-oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$-bis(aqua(nitrato-$\kappa O$){[1-(2-pyridyl-$\kappa N$)-ethylidene]hydrazine-$\kappa N$}copper(II)) $\mu$-oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$-bis-((methanol-$\kappa O$)(nitrato-$\kappa O$){[1-(2-pyridyl-$\kappa N$)ethylidene]hydrazine-$\kappa N$}-copper(II)) (1/1)

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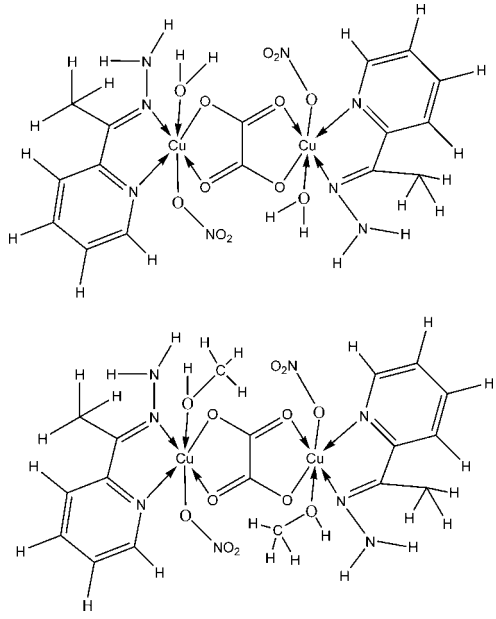
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.009 Å; $R$ factor = 0.059; $wR$ factor = 0.113; data-to-parameter ratio = 12.8.

The title cocrystal, $[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(H_2O)_2]$-$[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(CH_4O)_2]$, is a 1:1 cocrystal of two centrosymmetric $Cu^{II}$ complexes with oxalate dianions and Schiff base ligands. In each molecule, the $Cu^{II}$ centre is in a distorted octahedral *cis*-$CuN_2O_4$ environment, the donor atoms of the *N*,*N*′-bidentate Schiff base ligand and the bridging *O*,*O*′-bidentate oxalate group lying in the equatorial plane. In one molecule, a monodentate nitrate anion and a water molecule occupy the axial sites, and in the other, a monodentate nitrate anion and a methanol molecule occupy these sites. In the crystal structure, intermolecular N—H···O, O—H···O and N—H···N hydrogen bonds link the molecules into a network. Weak intramolecular N—H···O interactions are also observed.

## Related literature

For related structures: see Kelly *et al.* (2005); Bulut *et al.* (2005); Moreno *et al.* (2007); Du *et al.* (2007).



## Experimental

### Crystal data

$[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(H_2O)_2][Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(CH_4O)_2]$
$M_r$ = 1319.04
Triclinic, $P\overline{1}$
$a$ = 9.8358 (9) Å
$b$ = 12.3773 (10) Å
$c$ = 12.7136 (10) Å
$\alpha$ = 103.704 (4)°
$\beta$ = 112.573 (4)°
$\gamma$ = 107.821 (4)°
$V$ = 1245.15 (18) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 1.79 mm$^{-1}$
$T$ = 173 (2) K
0.03 × 0.02 × 0.02 mm

### Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
11826 measured reflections
4872 independent reflections
3644 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.057

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.112
$S$ = 1.06
4872 reflections
380 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.92 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.54 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—N1 | 1.966 (4) | Cu2—N5 | 1.955 (4) |
| Cu1—O1 | 1.986 (3) | Cu2—O7 | 1.966 (3) |
| Cu1—N2 | 1.991 (4) | Cu2—O8 | 1.981 (3) |
| Cu1—O2 | 2.000 (3) | Cu2—N6 | 1.994 (4) |
| Cu1—O3 | 2.252 (4) | Cu2—O9 | 2.337 (3) |
| Cu1—O4 | 2.610 (4) | Cu2—O10 | 2.541 (4) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H18···O11$^{i}$ | 0.96 (2) | 2.11 (3) | 3.048 (7) | 164 (5) |
| O3—H18···O12$^{i}$ | 0.96 (2) | 2.30 (4) | 3.084 (6) | 138 (5) |
| O3—H18···N8$^{i}$ | 0.96 (2) | 2.53 (2) | 3.471 (6) | 167 (5) |
| O3—H19···O9$^{ii}$ | 0.95 (2) | 1.85 (2) | 2.777 (5) | 165 (5) |
| N3—H20···O1 | 0.95 (2) | 2.53 (7) | 3.014 (6) | 112 (5) |
| N3—H21···O12 | 0.97 (2) | 2.44 (7) | 3.150 (7) | 130 (7) |
| N7—H22···O6 | 0.96 (2) | 2.35 (4) | 3.131 (6) | 138 (5) |
| N7—H23···N3 | 0.95 (2) | 2.43 (5) | 3.196 (7) | 138 (5) |
| N7—H23···O7 | 0.95 (2) | 2.59 (6) | 3.091 (5) | 113 (5) |
| O9—H24···O6$^{iii}$ | 0.84 | 1.89 | 2.731 (5) | 174 |
| O9—H24···N4$^{iii}$ | 0.84 | 2.57 | 3.367 (6) | 158 |
| O9—H24···O5$^{iii}$ | 0.84 | 2.56 | 3.171 (6) | 130 |

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Nonius, 1998); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); 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: HB2759).

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# supporting information

*Acta Cryst.* (2008). E**64**, m1124–m1125 [doi:10.1107/S1600536808024550]

# The cocrystal $\mu$-oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$-bis(aqua(nitrato-$\kappa O$){[1-(2-pyridyl-$\kappa N$)ethylidene]hydrazine-$\kappa N$}copper(II)) $\mu$-oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$-bis-((methanol-$\kappa O$)(nitrato-$\kappa O$){[1-(2-pyridyl-$\kappa N$)ethylidene]hydrazine-$\kappa N$}copper(II)) (1/1)

**Madina Diallo, Farba Bouyagui Tamboura, Mohamed Gaye, Aliou Hamady Barry and Youssouph Bah**

## S1. Comment

The molecular structure of the title compound, (I), (Fig. 1) contains two centrosymmetric binuclear $Cu^{II}$ complexes (A and B) with the same Schiff base ligand. The coordination spheres around $Cu^{II}$ in both A and B are slightly distorted octahedra (Table 1), with the coordination plane of each $Cu^{II}$ formed by the $N_2O_2$donor atoms of the Schiff base $N_2$ and the oxalate $O_2$. The axial positions in A are occupied by an O—$NO_2$ ion and a water molecule whereas in B these positions are occupied by a O-$NO_2$ ion and a $CH_3OH$ molecule. The in-plane Cu—O distances are in the range 1.966 (3)–2.000 (3) Å with Cu—N distances 1.955 (4)–1.994 (4) Å, which are slightly larger than distances observed in other $Cu^{II}$ coordination complexes of the same Schiff base ligand (Kelly et al <i\>., 2005). The elongation of the Cu—O—$NO_2$ and Cu—O(water) or Cu—O(methanol) axial bonds [2.610 (4) and 2.251 (4) Å in A and 2.541 (4) and 2.338 (3) Å in B] clearly indicate the usual Jahn Teller distortion of the $Cu^{II}$ as has been found previously (Bulut et al <i\>., 2005; Moreno et al <i\>., 2007; Du et al <i\>., 2007). The basal bond angles O–Cu–O and N–Cu–N are less then 90° [N1–Cu1–N2 = 80.63 (18) ° and N5–Cu2–N6 = 81.50 (17) °; O1–Cu1–O2 = 84.01 (13) ° and O7–Cu2–O8 = 85.09 (17) °] whereas the O–Cu–N angles are largely superior to 90° [N1–Cu1–O2 = 98.76 (16) ° and N2–Cu1–O1 =95.46 (16) ° in A; N5–Cu2–O8 = 95.29 (15) ° and N6–Cu2–O7 =97.93 (15) ° in B]. The axial bonds angles O(water)–Cu1–O—$NO_2$ and O(methanol)–Cu2–O—$NO_2$ are also less than the ideal value of 180° [168.34 (14) ° in A and 173.96 (12) ° in B]. A network of hydrogren bonds (Table 2) completes the structure.

## S2. Experimental

To a mixture of 0.324 g (1.0 mmol) of the ligand and 50 ml of methanol was added dropwise a solution of 0.463 g (2.0 mmol) of copper nitrate dihydrate in 10 ml of methanol. The resulting mixture was stirred under reflux for 120 min. After cooling the solution was left for slow evaporation and the title compound was obtained in good yield (0.620 g; 94.00°). IR ($cm^{-1}$,KBr): 1655, 1625, 1603, 1585, 1484, 1375, 1327, 1030, 829, 783, 699. Analysis calculated for $C_{34}H_{48}N_{16}O_{24}Cu_4$: C 30.96, H 3.67, N 16.99 °; found: C 30.94, H 3.69, N 16.95 °. Gren prisms of (I) were obtained from slow evaporation of a dimethylformamide solution.

## S3. Refinement

All water H atoms and amine H atoms of the bidentate Schiff base ligand were located from the difference fourier map and refined. The water O—H and amine N—H distances were restrained to be 0.96 Å, with s.u's of 0.02 Å. Others H

atoms were placed geometrically and refined with a riding model. $U_{iso}$(H) for H was assigned as 1.2 $U_{eq}$ of the attached C or N atoms (1.5 for methyl C atoms).

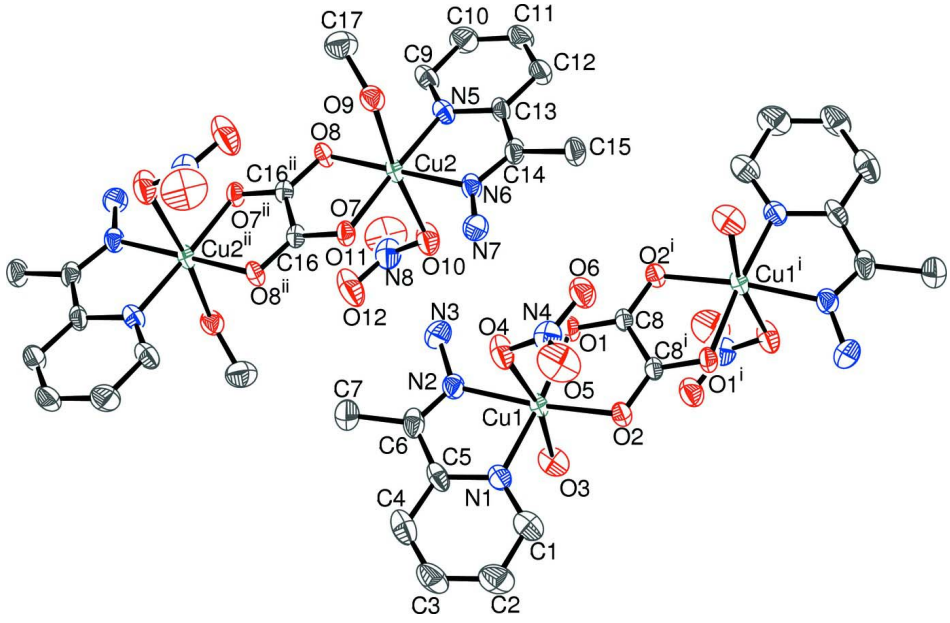


**Figure 1**

The molecular structure of (I) (H atoms are omitted for clarity). Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes: (i) -x, -y-1, -z-1; (ii) 2-x, -y, -z.

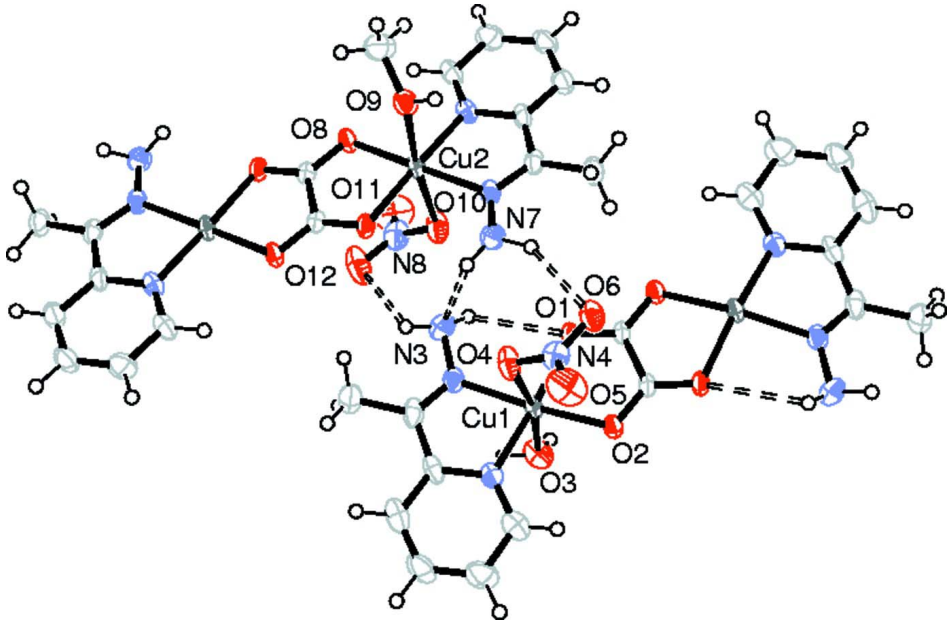


**Figure 2**

Part of the packing in (I) showing hydrogen bonds as broken lines.

**μ-oxalato-κ⁴O¹,O²:O¹′,O²′- bis(aqua(nitrato-κO){[1-(2-pyridyl-κN)ethylidene]hydrazine- κN}copper(II))–μ-oxalato- κ⁴O¹,O²:O¹′,O²′- bis((methanol-κO)(nitrato-κO){[1-(2-pyridyl- κN)ethylidene]hydrazine-κN}copper(II)) (1/1)**

*Crystal data*

$[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(H_2O)_2]$ $[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(CH_4O)_2]$
$M_r$ = 1319.04
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 9.8358 (9) Å
$b$ = 12.3773 (10) Å
$c$ = 12.7136 (10) Å
$\alpha$ = 103.704 (4)°
$\beta$ = 112.573 (4)°
$\gamma$ = 107.821 (4)°
$V$ = 1245.15 (18) Å$^3$
$Z$ = 1
$F(000)$ = 672
$D_x$ = 1.759 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 3872 reflections
$\theta$ = 1.0–26.0°
$\mu$ = 1.79 mm$^{-1}$
$T$ = 173 K
Prism, green
0.03 × 0.02 × 0.02 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\pi$ [IS PI CORRECT?] scans
11826 measured reflections
4872 independent reflections
3644 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.057
$\theta_{max}$ = 26.0°, $\theta_{min}$ = 1.9°
$h$ = −12→11
$k$ = −14→15
$l$ = −15→15

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.112
$S$ = 1.07
4872 reflections
380 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difmap and geom
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 3.8674P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.92 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.54 e Å$^{-3}$

*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)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.16109 (7) | −0.43205 (5) | −0.26049 (5) | 0.02519 (16) |
| Cu2 | 0.80107 (7) | −0.09303 (5) | −0.23584 (5) | 0.02536 (16) |

| | | | | |
|---|---|---|---|---|
| O1 | 0.1705 (4) | −0.3628 (3) | −0.3847 (3) | 0.0256 (7) |
| O2 | −0.0358 (4) | −0.5775 (3) | −0.4088 (3) | 0.0256 (7) |
| O3 | 0.0280 (5) | −0.3375 (4) | −0.1957 (4) | 0.0411 (9) |
| O4 | 0.3402 (5) | −0.5415 (4) | −0.2903 (3) | 0.0421 (9) |
| O5 | 0.2179 (6) | −0.7368 (4) | −0.4051 (4) | 0.0650 (13) |
| O6 | 0.2292 (5) | −0.6055 (3) | −0.4905 (3) | 0.0406 (9) |
| O7 | 0.8412 (4) | −0.1491 (3) | −0.0993 (3) | 0.0260 (7) |
| O8 | 0.9916 (4) | 0.0660 (3) | −0.1073 (3) | 0.0264 (7) |
| O9 | 0.9512 (4) | −0.1775 (3) | −0.3019 (3) | 0.0342 (8) |
| H24 | 0.8965 | −0.2413 | −0.3686 | 0.08 (3)* |
| O10 | 0.6195 (5) | −0.0053 (4) | −0.1877 (3) | 0.0470 (10) |
| O11 | 0.7199 (6) | 0.1888 (4) | −0.0798 (5) | 0.0727 (15) |
| O12 | 0.7466 (6) | 0.0644 (4) | 0.0110 (4) | 0.0639 (13) |
| N1 | 0.1741 (5) | −0.4997 (4) | −0.1337 (4) | 0.0303 (10) |
| N2 | 0.3849 (5) | −0.3083 (4) | −0.1229 (4) | 0.0306 (10) |
| N3 | 0.4829 (6) | −0.2153 (5) | −0.1376 (5) | 0.0483 (13) |
| N4 | 0.2618 (5) | −0.6290 (4) | −0.3950 (4) | 0.0343 (10) |
| N5 | 0.7526 (5) | −0.0355 (4) | −0.3705 (4) | 0.0287 (9) |
| N6 | 0.5987 (5) | −0.2449 (4) | −0.3691 (3) | 0.0277 (9) |
| N7 | 0.5443 (6) | −0.3515 (4) | −0.3500 (4) | 0.0345 (10) |
| N8 | 0.6948 (6) | 0.0835 (5) | −0.0856 (4) | 0.0415 (12) |
| C1 | 0.0535 (8) | −0.5935 (5) | −0.1446 (5) | 0.0396 (13) |
| H1 | −0.0475 | −0.6368 | −0.2208 | 0.048* |
| C2 | 0.0702 (9) | −0.6314 (5) | −0.0462 (6) | 0.0503 (16) |
| H2 | −0.0178 | −0.6988 | −0.0545 | 0.060* |
| C3 | 0.2192 (8) | −0.5670 (5) | 0.0630 (5) | 0.0472 (15) |
| H3 | 0.2353 | −0.5910 | 0.1308 | 0.057* |
| C4 | 0.3432 (8) | −0.4695 (6) | 0.0739 (5) | 0.0468 (15) |
| H4 | 0.4456 | −0.4256 | 0.1490 | 0.056* |
| C5 | 0.3192 (7) | −0.4341 (5) | −0.0259 (4) | 0.0316 (12) |
| C6 | 0.4383 (6) | −0.3281 (5) | −0.0245 (5) | 0.0362 (13) |
| C7 | 0.6073 (7) | −0.2464 (6) | 0.0880 (5) | 0.0503 (16) |
| H7A | 0.6882 | −0.2226 | 0.0606 | 0.076* |
| H7B | 0.6354 | −0.2921 | 0.1398 | 0.076* |
| H7C | 0.6076 | −0.1718 | 0.1366 | 0.076* |
| C8 | 0.0597 (6) | −0.4386 (4) | −0.4928 (4) | 0.0221 (10) |
| C9 | 0.8353 (7) | 0.0747 (5) | −0.3624 (5) | 0.0346 (12) |
| H9 | 0.9293 | 0.1336 | −0.2851 | 0.042* |
| C10 | 0.7900 (7) | 0.1081 (5) | −0.4626 (5) | 0.0425 (14) |
| H10 | 0.8512 | 0.1884 | −0.4548 | 0.051* |
| C11 | 0.6536 (7) | 0.0212 (6) | −0.5740 (5) | 0.0414 (14) |
| H11 | 0.6201 | 0.0418 | −0.6442 | 0.050* |
| C12 | 0.5649 (7) | −0.0957 (5) | −0.5847 (5) | 0.0374 (13) |
| H12 | 0.4699 | −0.1549 | −0.6613 | 0.045* |
| C13 | 0.6171 (6) | −0.1254 (5) | −0.4813 (4) | 0.0292 (11) |
| C14 | 0.5375 (6) | −0.2435 (5) | −0.4771 (4) | 0.0288 (11) |
| C15 | 0.3982 (6) | −0.3556 (5) | −0.5918 (5) | 0.0392 (13) |
| H15A | 0.4234 | −0.4267 | −0.5971 | 0.059* |

| | | | | |
|---|---|---|---|---|
| H15B | 0.3837 | −0.3385 | −0.6659 | 0.059* |
| H15C | 0.2969 | −0.3744 | −0.5871 | 0.059* |
| C16 | 0.9575 (5) | −0.0615 (4) | 0.0021 (4) | 0.0217 (10) |
| C17 | 1.0924 (8) | −0.0986 (6) | −0.2984 (6) | 0.0484 (15) |
| H17A | 1.0615 | −0.0565 | −0.3535 | 0.073* |
| H17B | 1.1430 | −0.1476 | −0.3263 | 0.073* |
| H17C | 1.1708 | −0.0368 | −0.2131 | 0.073* |
| H18 | 0.107 (6) | −0.277 (4) | −0.112 (3) | 0.058 (19)* |
| H19 | −0.001 (7) | −0.277 (4) | −0.220 (5) | 0.050 (17)* |
| H20 | 0.418 (8) | −0.186 (6) | −0.190 (5) | 0.09 (3)* |
| H21 | 0.570 (7) | −0.154 (6) | −0.055 (4) | 0.12 (3)* |
| H22 | 0.437 (4) | −0.406 (4) | −0.420 (4) | 0.055 (18)* |
| H23 | 0.559 (8) | −0.332 (6) | −0.268 (3) | 0.07 (2)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0265 (3) | 0.0263 (3) | 0.0162 (3) | 0.0107 (3) | 0.0062 (3) | 0.0068 (3) |
| Cu2 | 0.0265 (3) | 0.0248 (3) | 0.0155 (3) | 0.0102 (3) | 0.0045 (3) | 0.0052 (2) |
| O1 | 0.0230 (18) | 0.0232 (17) | 0.0179 (17) | 0.0062 (15) | 0.0039 (15) | 0.0045 (14) |
| O2 | 0.0258 (18) | 0.0257 (18) | 0.0199 (17) | 0.0103 (15) | 0.0074 (15) | 0.0088 (14) |
| O3 | 0.056 (3) | 0.041 (2) | 0.042 (2) | 0.033 (2) | 0.028 (2) | 0.020 (2) |
| O4 | 0.042 (2) | 0.048 (2) | 0.024 (2) | 0.024 (2) | 0.0072 (18) | 0.0050 (18) |
| O5 | 0.096 (4) | 0.041 (3) | 0.067 (3) | 0.034 (3) | 0.045 (3) | 0.023 (2) |
| O6 | 0.042 (2) | 0.043 (2) | 0.027 (2) | 0.0173 (19) | 0.0132 (18) | 0.0070 (17) |
| O7 | 0.0223 (18) | 0.0228 (17) | 0.0191 (17) | 0.0053 (15) | 0.0038 (15) | 0.0042 (14) |
| O8 | 0.0283 (19) | 0.0267 (18) | 0.0164 (16) | 0.0106 (16) | 0.0054 (15) | 0.0082 (14) |
| O9 | 0.035 (2) | 0.038 (2) | 0.026 (2) | 0.0173 (18) | 0.0145 (17) | 0.0090 (18) |
| O10 | 0.041 (2) | 0.052 (3) | 0.029 (2) | 0.021 (2) | 0.0076 (19) | 0.0044 (19) |
| O11 | 0.095 (4) | 0.042 (3) | 0.098 (4) | 0.040 (3) | 0.057 (4) | 0.025 (3) |
| O12 | 0.071 (3) | 0.078 (3) | 0.027 (2) | 0.039 (3) | 0.012 (2) | 0.010 (2) |
| N1 | 0.031 (2) | 0.035 (2) | 0.025 (2) | 0.017 (2) | 0.013 (2) | 0.0117 (19) |
| N2 | 0.027 (2) | 0.034 (2) | 0.023 (2) | 0.012 (2) | 0.011 (2) | 0.0039 (19) |
| N3 | 0.034 (3) | 0.044 (3) | 0.042 (3) | −0.001 (3) | 0.015 (3) | 0.010 (3) |
| N4 | 0.034 (3) | 0.034 (3) | 0.040 (3) | 0.022 (2) | 0.018 (2) | 0.013 (2) |
| N5 | 0.034 (2) | 0.032 (2) | 0.022 (2) | 0.019 (2) | 0.012 (2) | 0.0122 (19) |
| N6 | 0.025 (2) | 0.031 (2) | 0.020 (2) | 0.013 (2) | 0.0076 (19) | 0.0025 (18) |
| N7 | 0.033 (3) | 0.027 (2) | 0.032 (3) | 0.006 (2) | 0.014 (2) | 0.008 (2) |
| N8 | 0.038 (3) | 0.045 (3) | 0.040 (3) | 0.026 (2) | 0.017 (2) | 0.007 (2) |
| C1 | 0.052 (4) | 0.041 (3) | 0.035 (3) | 0.028 (3) | 0.023 (3) | 0.017 (3) |
| C2 | 0.069 (5) | 0.035 (3) | 0.052 (4) | 0.019 (3) | 0.033 (4) | 0.026 (3) |
| C3 | 0.067 (4) | 0.040 (3) | 0.036 (3) | 0.023 (3) | 0.022 (3) | 0.025 (3) |
| C4 | 0.051 (4) | 0.057 (4) | 0.029 (3) | 0.032 (3) | 0.011 (3) | 0.016 (3) |
| C5 | 0.038 (3) | 0.043 (3) | 0.018 (2) | 0.029 (3) | 0.011 (2) | 0.009 (2) |
| C6 | 0.028 (3) | 0.043 (3) | 0.023 (3) | 0.017 (3) | 0.008 (2) | −0.002 (2) |
| C7 | 0.034 (3) | 0.066 (4) | 0.035 (3) | 0.015 (3) | 0.011 (3) | 0.014 (3) |
| C8 | 0.019 (2) | 0.024 (2) | 0.017 (2) | 0.010 (2) | 0.006 (2) | 0.005 (2) |
| C9 | 0.042 (3) | 0.043 (3) | 0.025 (3) | 0.025 (3) | 0.015 (3) | 0.018 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C10 | 0.047 (4) | 0.043 (3) | 0.046 (3) | 0.021 (3) | 0.025 (3) | 0.028 (3) |
| C11 | 0.043 (3) | 0.064 (4) | 0.034 (3) | 0.031 (3) | 0.021 (3) | 0.032 (3) |
| C12 | 0.034 (3) | 0.053 (4) | 0.026 (3) | 0.022 (3) | 0.013 (3) | 0.018 (3) |
| C13 | 0.024 (3) | 0.044 (3) | 0.019 (2) | 0.021 (2) | 0.007 (2) | 0.010 (2) |
| C14 | 0.023 (3) | 0.032 (3) | 0.022 (3) | 0.012 (2) | 0.007 (2) | 0.002 (2) |
| C15 | 0.030 (3) | 0.046 (3) | 0.023 (3) | 0.012 (3) | 0.007 (2) | 0.003 (2) |
| C16 | 0.020 (2) | 0.021 (2) | 0.021 (2) | 0.010 (2) | 0.007 (2) | 0.005 (2) |
| C17 | 0.051 (4) | 0.046 (4) | 0.052 (4) | 0.017 (3) | 0.031 (3) | 0.021 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—N1 | 1.966 (4) | N7—H22 | 0.96 (2) |
| Cu1—O1 | 1.986 (3) | N7—H23 | 0.95 (2) |
| Cu1—N2 | 1.991 (4) | C1—C2 | 1.406 (8) |
| Cu1—O2 | 2.000 (3) | C1—H1 | 0.9500 |
| Cu1—O3 | 2.252 (4) | C2—C3 | 1.382 (9) |
| Cu1—O4 | 2.610 (4) | C2—H2 | 0.9500 |
| Cu2—N5 | 1.955 (4) | C3—C4 | 1.362 (8) |
| Cu2—O7 | 1.966 (3) | C3—H3 | 0.9500 |
| Cu2—O8 | 1.981 (3) | C4—C5 | 1.397 (7) |
| Cu2—N6 | 1.994 (4) | C4—H4 | 0.9500 |
| Cu2—O9 | 2.337 (3) | C5—C6 | 1.458 (8) |
| Cu2—O10 | 2.541 (4) | C6—C7 | 1.514 (7) |
| O1—C8 | 1.254 (5) | C7—H7A | 0.9800 |
| O2—C8$^{i}$ | 1.258 (5) | C7—H7B | 0.9800 |
| O3—H18 | 0.96 (2) | C7—H7C | 0.9800 |
| O3—H19 | 0.95 (2) | C8—O2$^{i}$ | 1.258 (5) |
| O4—N4 | 1.248 (5) | C8—C8$^{i}$ | 1.527 (9) |
| O5—N4 | 1.227 (6) | C9—C10 | 1.386 (7) |
| O6—N4 | 1.260 (5) | C9—H9 | 0.9500 |
| O7—C16 | 1.262 (5) | C10—C11 | 1.378 (8) |
| O8—C16$^{ii}$ | 1.258 (5) | C10—H10 | 0.9500 |
| O9—C17 | 1.409 (6) | C11—C12 | 1.384 (8) |
| O9—H24 | 0.8400 | C11—H11 | 0.9500 |
| O10—N8 | 1.237 (5) | C12—C13 | 1.398 (7) |
| O11—N8 | 1.228 (6) | C12—H12 | 0.9500 |
| O12—N8 | 1.247 (6) | C13—C14 | 1.457 (7) |
| N1—C1 | 1.315 (7) | C14—C15 | 1.508 (7) |
| N1—C5 | 1.356 (6) | C15—H15A | 0.9800 |
| N2—C6 | 1.273 (7) | C15—H15B | 0.9800 |
| N2—N3 | 1.360 (6) | C15—H15C | 0.9800 |
| N3—H20 | 0.95 (2) | C16—O8$^{ii}$ | 1.258 (5) |
| N3—H21 | 0.97 (2) | C16—C16$^{ii}$ | 1.520 (9) |
| N5—C9 | 1.313 (7) | C17—H17A | 0.9800 |
| N5—C13 | 1.381 (6) | C17—H17B | 0.9800 |
| N6—C14 | 1.277 (6) | C17—H17C | 0.9800 |
| N6—N7 | 1.381 (6) | | |

| | | | |
|---|---|---|---|
| N1—Cu1—O1 | 174.12 (15) | O11—N8—O10 | 120.4 (5) |
| N1—Cu1—N2 | 80.65 (18) | O11—N8—O12 | 120.7 (5) |
| O1—Cu1—N2 | 95.44 (16) | O10—N8—O12 | 118.9 (5) |
| N1—Cu1—O2 | 98.76 (16) | N1—C1—C2 | 121.7 (6) |
| O1—Cu1—O2 | 84.01 (13) | N1—C1—H1 | 119.2 |
| N2—Cu1—O2 | 166.68 (14) | C2—C1—H1 | 119.2 |
| N1—Cu1—O3 | 86.33 (15) | C3—C2—C1 | 117.6 (6) |
| O1—Cu1—O3 | 98.48 (13) | C3—C2—H2 | 121.2 |
| N2—Cu1—O3 | 95.43 (16) | C1—C2—H2 | 121.2 |
| O2—Cu1—O3 | 97.82 (14) | C4—C3—C2 | 120.4 (5) |
| N1—Cu1—O4 | 83.01 (14) | C4—C3—H3 | 119.8 |
| O1—Cu1—O4 | 91.90 (12) | C2—C3—H3 | 119.8 |
| N2—Cu1—O4 | 78.20 (14) | C3—C4—C5 | 119.7 (6) |
| O2—Cu1—O4 | 88.50 (12) | C3—C4—H4 | 120.1 |
| O3—Cu1—O4 | 168.33 (13) | C5—C4—H4 | 120.1 |
| N5—Cu2—O7 | 177.14 (15) | N1—C5—C4 | 119.5 (5) |
| N5—Cu2—O8 | 95.30 (15) | N1—C5—C6 | 115.2 (4) |
| O7—Cu2—O8 | 85.09 (13) | C4—C5—C6 | 125.3 (5) |
| N5—Cu2—N6 | 81.51 (17) | N2—C6—C5 | 114.2 (4) |
| O7—Cu2—N6 | 97.92 (15) | N2—C6—C7 | 123.9 (5) |
| O8—Cu2—N6 | 175.14 (15) | C5—C6—C7 | 121.8 (5) |
| N5—Cu2—O9 | 89.35 (14) | C6—C7—H7A | 109.5 |
| O7—Cu2—O9 | 93.43 (13) | C6—C7—H7B | 109.5 |
| O8—Cu2—O9 | 95.95 (13) | H7A—C7—H7B | 109.5 |
| N6—Cu2—O9 | 87.70 (14) | C6—C7—H7C | 109.5 |
| N5—Cu2—O10 | 85.40 (14) | H7A—C7—H7C | 109.5 |
| O7—Cu2—O10 | 91.78 (13) | H7B—C7—H7C | 109.5 |
| O8—Cu2—O10 | 87.50 (13) | O1—C8—O2$^{i}$ | 126.0 (4) |
| N6—Cu2—O10 | 88.58 (14) | O1—C8—C8$^{i}$ | 117.4 (5) |
| O9—Cu2—O10 | 173.97 (12) | O2$^{i}$—C8—C8$^{i}$ | 116.6 (5) |
| C8—O1—Cu1 | 111.0 (3) | N5—C9—C10 | 122.3 (5) |
| C8$^{i}$—O2—Cu1 | 110.9 (3) | N5—C9—H9 | 118.9 |
| Cu1—O3—H18 | 106 (4) | C10—C9—H9 | 118.9 |
| Cu1—O3—H19 | 126 (3) | C11—C10—C9 | 118.0 (5) |
| H18—O3—H19 | 92 (5) | C11—C10—H10 | 121.0 |
| N4—O4—Cu1 | 110.5 (3) | C9—C10—H10 | 121.0 |
| C16—O7—Cu2 | 110.2 (3) | C10—C11—C12 | 120.7 (5) |
| C16$^{ii}$—O8—Cu2 | 110.3 (3) | C10—C11—H11 | 119.7 |
| C17—O9—Cu2 | 119.5 (3) | C12—C11—H11 | 119.7 |
| C17—O9—H24 | 109.5 | C11—C12—C13 | 119.1 (5) |
| Cu2—O9—H24 | 116.3 | C11—C12—H12 | 120.4 |
| N8—O10—Cu2 | 113.3 (3) | C13—C12—H12 | 120.4 |
| C1—N1—C5 | 121.1 (5) | N5—C13—C12 | 118.7 (5) |
| C1—N1—Cu1 | 125.4 (4) | N5—C13—C14 | 115.4 (4) |
| C5—N1—Cu1 | 113.4 (3) | C12—C13—C14 | 125.9 (5) |
| C6—N2—N3 | 121.3 (5) | N6—C14—C13 | 114.4 (4) |
| C6—N2—Cu1 | 116.4 (4) | N6—C14—C15 | 123.1 (5) |
| N3—N2—Cu1 | 122.0 (3) | C13—C14—C15 | 122.5 (4) |

| | | | |
|---|---|---|---|
| N2—N3—H20 | 110 (5) | C14—C15—H15A | 109.5 |
| N2—N3—H21 | 108 (5) | C14—C15—H15B | 109.5 |
| H20—N3—H21 | 116 (7) | H15A—C15—H15B | 109.5 |
| O5—N4—O4 | 120.6 (5) | C14—C15—H15C | 109.5 |
| O5—N4—O6 | 120.2 (5) | H15A—C15—H15C | 109.5 |
| O4—N4—O6 | 119.2 (4) | H15B—C15—H15C | 109.5 |
| C9—N5—C13 | 121.2 (4) | O8$^{ii}$—C16—O7 | 125.8 (4) |
| C9—N5—Cu2 | 126.3 (3) | O8$^{ii}$—C16—C16$^{ii}$ | 116.7 (5) |
| C13—N5—Cu2 | 112.6 (3) | O7—C16—C16$^{ii}$ | 117.6 (5) |
| C14—N6—N7 | 121.9 (4) | O9—C17—H17A | 109.5 |
| C14—N6—Cu2 | 115.9 (4) | O9—C17—H17B | 109.5 |
| N7—N6—Cu2 | 121.5 (3) | H17A—C17—H17B | 109.5 |
| N6—N7—H22 | 106 (4) | O9—C17—H17C | 109.5 |
| N6—N7—H23 | 111 (4) | H17A—C17—H17C | 109.5 |
| H22—N7—H23 | 119 (5) | H17B—C17—H17C | 109.5 |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H18···O11$^{iii}$ | 0.96 (2) | 2.11 (3) | 3.048 (7) | 164 (5) |
| O3—H18···O12$^{iii}$ | 0.96 (2) | 2.30 (4) | 3.084 (6) | 138 (5) |
| O3—H18···N8$^{iii}$ | 0.96 (2) | 2.53 (2) | 3.471 (6) | 167 (5) |
| O3—H19···O9$^{iv}$ | 0.95 (2) | 1.85 (2) | 2.777 (5) | 165 (5) |
| N3—H20···O1 | 0.95 (2) | 2.53 (7) | 3.014 (6) | 112 (5) |
| N3—H21···O12 | 0.97 (2) | 2.44 (7) | 3.150 (7) | 130 (7) |
| N7—H22···O6 | 0.96 (2) | 2.35 (4) | 3.131 (6) | 138 (5) |
| N7—H23···N3 | 0.95 (2) | 2.43 (5) | 3.196 (7) | 138 (5) |
| N7—H23···O7 | 0.95 (2) | 2.59 (6) | 3.091 (5) | 113 (5) |
| O9—H24···O6$^{v}$ | 0.84 | 1.89 | 2.731 (5) | 174 |
| O9—H24···N4$^{v}$ | 0.84 | 2.57 | 3.367 (6) | 158 |
| O9—H24···O5$^{v}$ | 0.84 | 2.56 | 3.171 (6) | 130 |

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