

The cocrystal μ -oxalato- $\kappa^4O^1,O^2:O^1',O^2'$ -bis(aqua(nitrato- κO)[1-(2-pyridyl- κN)-ethylidene]hydrazine- κN]copper(II) μ -oxalato- $\kappa^4O^1,O^2:O^1',O^2'$ -bis((methanol- κO)(nitrato- κO)[1-(2-pyridyl- κN)ethylidene]hydrazine- κN]-copper(II) (1/1)

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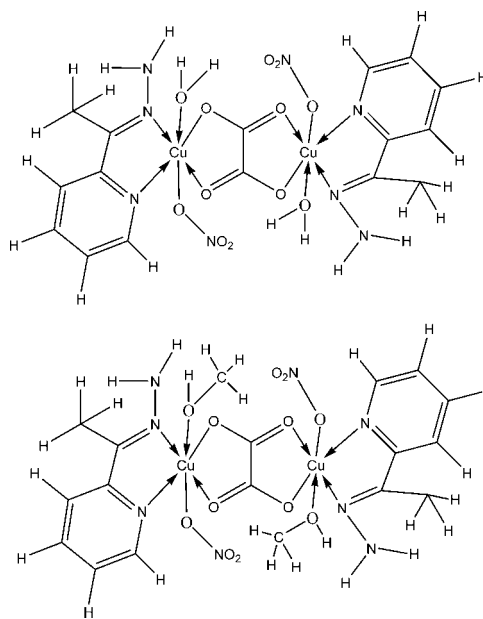
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(C-C) = 0.009$ Å; R factor = 0.059; wR factor = 0.113; data-to-parameter ratio = 12.8.

The title cocrystal, $[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(H_2O)_2] \cdot [Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2(CH_4O)_2]$, 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 $N-H \cdots O$, $O-H \cdots O$ and $N-H \cdots N$ hydrogen bonds link the molecules into a network. Weak intramolecular $N-H \cdots O$ 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

$[Cu_2(C_2O_4)(NO_3)_2(C_7H_9N_3)_2 \cdot (H_2O)_2] \cdot [Cu_2(C_2O_4)(NO_3)_2 \cdot (C_7H_9N_3)_2(CH_4O)_2]$
 $M_r = 1319.04$
Triclinic, $P\bar{1}$
 $a = 9.8358$ (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) Å³
 $Z = 1$
Mo $K\alpha$ radiation
 $\mu = 1.79$ mm⁻¹
 $T = 173$ (2) K
 $0.03 \times 0.02 \times 0.02$ 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, °).

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

Acta Cryst. (2008). E64, m1124-m1125 [doi:10.1107/S1600536808024550]

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

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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>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>et al</i>, 2005; Moreno et al <i>et al</i>, 2007; Du et al <i>et al</i>, 2007). The basal bond angles $O-Cu-O$ and $N-Cu-N$ are less than 90° [$N1-Cu1-N2 = 80.63 (18)^\circ$ and $N5-Cu2-N6 = 81.50 (17)^\circ$; $O1-Cu1-O2 = 84.01 (13)^\circ$ and $O7-Cu2-O8 = 85.09 (17)^\circ$] whereas the $O-Cu-N$ angles are largely superior to 90° [$N1-Cu1-O2 = 98.76 (16)^\circ$ and $N2-Cu1-O1 = 95.46 (16)^\circ$ in A; $N5-Cu2-O8 = 95.29 (15)^\circ$ and $N6-Cu2-O7 = 97.93 (15)^\circ$ 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° [$168.34 (14)^\circ$ in A and $173.96 (12)^\circ$ in B]. A network of hydrogen bonds (Table 2) completes the structure.

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 %. Green prisms of (I) were obtained from slow evaporation of a dimethylformamide solution.

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. Other 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).

Figures

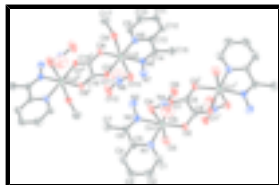


Fig. 1. The molecular structure of (I) (H atoms are omitted for clarity). Displacement ellipsoids are plotted at the 50% probability level. Symmetry codes: (i) $-x, -y-1, -z-1$; (ii) $2-x, -y, -z$.

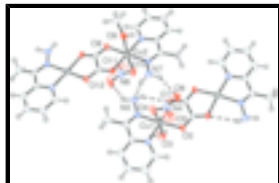


Fig. 2. Part of the packing in (I) showing hydrogen bonds as broken lines.

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Crystal data

$[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{C}_7\text{H}_9\text{N}_3)_2(\text{H}_2\text{O})_2]$

$[\text{Cu}_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{C}_7\text{H}_9\text{N}_3)_2(\text{CH}_4\text{O})_2]$

$M_r = 1319.04$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 9.8358\ (9)\ \text{\AA}$

$b = 12.3773\ (10)\ \text{\AA}$

$c = 12.7136\ (10)\ \text{\AA}$

$\alpha = 103.704\ (4)^\circ$

$\beta = 112.573\ (4)^\circ$

$\gamma = 107.821\ (4)^\circ$

$V = 1245.15\ (18)\ \text{\AA}^3$

$Z = 1$

$F_{000} = 672$

$D_x = 1.759\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3872 reflections

$\theta = 1.0\text{--}26.0^\circ$

$\mu = 1.79\ \text{mm}^{-1}$

$T = 173\ (2)\ \text{K}$

Prism, green

$0.03 \times 0.02 \times 0.02\ \text{mm}$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173\ (2)\ \text{K}$

π [IS PI CORRECT?] scans

Absorption correction: none

11826 measured reflections

4872 independent reflections

3644 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 1.9^\circ$

$h = -12 \rightarrow 11$

$k = -14 \rightarrow 15$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap and geom
$R[F^2 > 2\sigma(F^2)] = 0.059$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.112$	$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 3.8674P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
4872 reflections	$(\Delta/\sigma)_{\max} = 0.009$
380 parameters	$\Delta\rho_{\max} = 0.92 \text{ e } \text{\AA}^{-3}$
6 restraints	$\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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)

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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 (\AA^2)

	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 (\AA , $^\circ$)

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)

supplementary materials

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

supplementary materials

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

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

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

Fig. 1

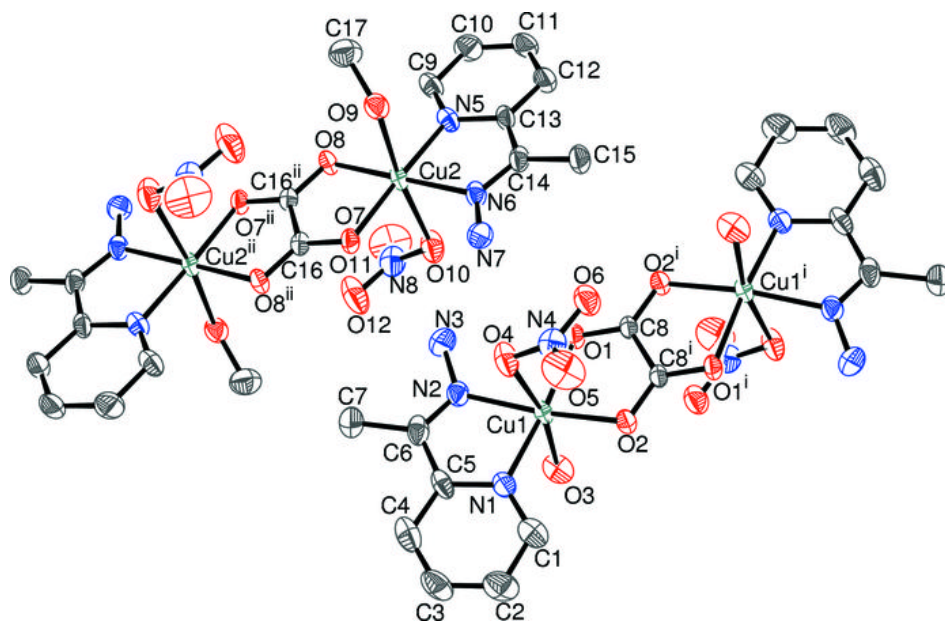


Fig. 2

