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(Methyl (*S*)-3-(imidazol-4-yl)-2-{6-[(*S*)-2-(imidazol-4-yl)-1-(methoxycarbonyl)-ethylaminocarbonyl]pyridine-2-carbonyl-amino}propionato)copper(II) methanol sesquisolvate

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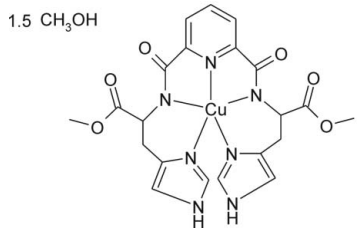
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.005 Å; disorder in solvent or counterion; R factor = 0.045; wR factor = 0.101; data-to-parameter ratio = 16.3.

In the Cu^{II} title complex, $[Cu(C_{21}H_{21}N_7O_6)]\cdot 1.5CH_4O$, two independent half-molecules of the title complex and one and a half methanol solvent molecules are in the asymmetric unit. The title complex possesses crystallographic C_2 symmetry. One methanol molecule is disordered around a twofold axis. The title complex geometry agrees well with that of the dihydrate determined earlier with the exception of an N—Cu—N angle deviating by almost 10°. The Cu^{II} centre is in a distorted square-pyramidal geometry, and intermolecular hydrogen bonds stabilize the molecular packing.

Related literature

For the dihydrate crystal structure determined earlier, see Otsuka *et al.* (1996); Kurosaki *et al.* (2001).

For related literature, see: An *et al.* (2003); Kottke & Stalke (1993); Moriuchi *et al.* (2001); Ryono & Weller (1987).



Experimental

Crystal data

$[Cu(C_{21}H_{21}N_7O_6)]\cdot 1.5CH_4O$
M_r = 577.04
Orthorhombic, $P2_12_12$
a = 13.701 (1) Å
b = 13.771 (1) Å
c = 13.590 (2) Å
V = 2564.1 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.91 mm^{-1}
T = 173 (2) K
0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.772, T_{max} = 0.839
23034 measured reflections
5867 independent reflections
4185 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.101
S = 0.92
5867 reflections
359 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}
Absolute structure: Flack (1983), 2561 Friedel pairs
Flack parameter: −0.012 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1^{i}	0.88	1.86	2.719 (4)	166
N7—H7···O4^{ii}	0.88	1.88	2.738 (4)	163
O11—H11A···O5^{iii}	0.84	2.00	2.785 (4)	155

Symmetry codes: (i) $x-\frac{1}{2}, -y-\frac{1}{2}, -z+1$; (ii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+2$; (iii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+1$.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: CS2055).

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supplementary materials

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(Methyl (*S*)-3-(imidazol-4-yl)-2-{6-[(*S*)-2-(imidazol-4-yl)-1-(methoxycarbonyl)ethylaminocarbonyl]pyridine-2-carbonylamino}propionato)copper(II) methanol sesquisolvate

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Comment

The title complex with one and a half methanol solvates crystallized in $P2_12_12$ space group having two independent half molecules in the asymmetric unit sitting on a crystallographic C_2 symmetry axes. Cu1, N1, C3 atoms of the one molecule and Cu2, N5 and C14 of the other molecule lie on 2-fold axes. The methanol molecule O12—C201 with site occupation factor 0.5 is disordered about a 2-fold axis. The same complex in dihydrate form instead of methanol has been previously found to crystallize in the $P4_32_12$ space group (Otsuka *et al.*, 1996, Kurosaki *et al.*, 2001). In both complexes, geometry around a five coordinated Cu(II) cation is a distorted square pyramid (Figure 1). The measured bond lengths and angles of the title complex agree well with the values obtained for the previously determined structure (Kurosaki *et al.*, 2001) with one exception. The N1—Cu1—N4 angle of the title complex differs as much as 9.85° less from the corresponding angle of the previously determined complex. Several intermolecular hydrogen bonds stabilize the molecular packing of the title complex.

Experimental

The title complex (4) was synthesized according to literature procedures. For the ligand synthesis, 2,6-pyridinedicarbonyl dichloride (1) (An *et al.*, 2003) and *L*-histidine methyl ester dihydrochloride (2) (Ryono & Weller, 1987) were prepared by reacting $SOCl_2$ with 2,6-pyridinedicarboxylic acid and *L*-histidine, respectively. Ligand (3) of the title complex was synthesized by coupling 1 and 2 (Moriuchi *et al.*, 2001). Finally, 4 was synthesized at room temperature by adding a MeOH solution of $(CH_3COO)_2Cu{\cdot}H_2O$ (0.066 g, 0.33 mmol) into a MeOH solution of 3 (0.155 g, 0.33 mmol) and stirring the blue solution formed for 70 h. After solvent removal in a vacuum, the complex was obtained as a blue powder (Kurosaki *et al.*, 2001). Blue crystals of the title compound, suitable for X-ray analysis, were obtained from a saturated solution of MeOH–MeCN (2:1).

Refinement

The crystal selected for the X-ray measurement at 173 K was mounted on a glass fibre using the oil drop method (Kottke & Stalke, 1993). H atoms were introduced in their calculated positions (*X*—H = 0.84, 0.88, 0.95, 0.98, 0.99, or 1.00 Å, U_{iso}=1.2 times the U_{eq} of the carrier atom and U_{iso}=1.5 times the U_{eq} of the carrier atom for methyl and OH H atoms) and were kept riding with fixed geometry with respect to their carrier atoms. No H atom positions were identified for the disordered methanol molecule.

Figures

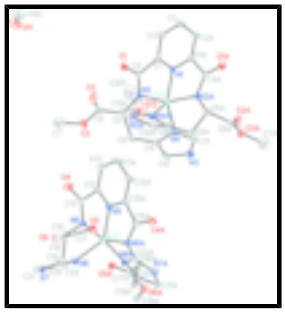


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for the sake of clarity.

(Methyl (S)-3-(imidazol-4-yl)-\ 2-{6-[(*S*)-2-(imidazol-4-yl)-1-(methoxycarbonyl)ethylaminocarbonyl]pyridine-\ 2-carbonylamino}propionato)copper(II) methanol sesquisolvate

Crystal data

$[Cu(C_{21}H_{21}N_7O_6)]\cdot 1.5CH_4O$	F_{000} = 1192
M_r = 577.04	D_x = 1.495 Mg m^{-3}
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2 2ab	Cell parameters from 23034 reflections
a = 13.701 (1) Å	θ = 3.3–27.5º
b = 13.771 (1) Å	μ = 0.91 mm^{-1}
c = 13.590 (2) Å	T = 173 (2) K
V = 2564.1 (5) Å^3	Block, blue
Z = 4	0.30 × 0.20 × 0.20 mm

Data collection

KappaCCD diffractometer	5867 independent reflections
Radiation source: fine-focus sealed tube	4185 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.064
T = 173(2) K	θ_{max} = 27.5º
ω and φ scans	θ_{min} = 3.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −17→17
T_{min} = 0.772, T_{max} = 0.839	k = −17→17
23034 measured reflections	l = −17→17

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.3474P]$ where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.92$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
5867 reflections	$\Delta\rho_{min} = -0.50$ e Å^{-3}
359 parameters	Extinction correction: none
2 restraints	Absolute structure: Flack (1983)
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.012 (16)
Secondary atom site location: difference Fourier map	

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	−0.5000	−0.5000	0.48333 (4)	0.02001 (14)	
O1	−0.3638 (2)	−0.28347 (19)	0.32677 (19)	0.0349 (7)	
N1	−0.5000	−0.5000	0.3408 (2)	0.0191 (8)	
C1	−0.4520 (2)	−0.4300 (2)	0.2937 (3)	0.0214 (8)	
N2	−0.4164 (2)	−0.38220 (19)	0.4561 (2)	0.0223 (7)	
Cu2	−0.5000	0.0000	1.00029 (3)	0.01894 (14)	
C2	−0.4508 (3)	−0.4272 (3)	0.1921 (3)	0.0291 (9)	
H2	−0.4174	−0.3771	0.1579	0.035*	
O2	−0.2196 (2)	−0.3824 (2)	0.5169 (2)	0.0485 (8)	
N3	−0.6990 (2)	−0.3186 (2)	0.6318 (2)	0.0303 (8)	
H3	−0.7571	−0.2948	0.6451	0.036*	
O3	−0.2429 (2)	−0.2419 (2)	0.5985 (2)	0.0480 (9)	
C3	−0.5000	−0.5000	0.1414 (3)	0.0376 (13)	
H3A	−0.5000	−0.5000	0.0715	0.045*	
N4	−0.5842 (2)	−0.4186 (2)	0.5793 (2)	0.0236 (7)	
C4	−0.4052 (3)	−0.3578 (2)	0.3633 (3)	0.0234 (8)	
O4	−0.26885 (19)	−0.11115 (17)	0.84523 (18)	0.0309 (6)	
N5	−0.5000	0.0000	0.8564 (2)	0.0216 (8)	
O5	−0.35581 (18)	−0.26385 (17)	1.03435 (18)	0.0287 (6)	
C5	−0.3818 (3)	−0.3123 (3)	0.5292 (3)	0.0298 (9)	
H5	−0.3986	−0.2453	0.5066	0.036*	
O6	−0.21054 (19)	−0.23048 (17)	1.10423 (18)	0.0281 (6)	
C6	−0.2722 (3)	−0.3190 (3)	0.5447 (3)	0.0367 (10)	
N6	−0.3735 (2)	−0.07025 (18)	0.9725 (2)	0.0190 (6)	
N7	−0.3301 (2)	0.2171 (2)	1.1365 (2)	0.0247 (7)	
H7	−0.3101	0.2773	1.1444	0.030*	
C7	−0.1386 (3)	−0.2378 (4)	0.6201 (3)	0.0720 (18)	
H7A	−0.1198	−0.2951	0.6584	0.108*	
H7B	−0.1243	−0.1789	0.6580	0.108*	
H7C	−0.1018	−0.2365	0.5583	0.108*	
N8	−0.4247 (2)	0.09291 (19)	1.0957 (2)	0.0197 (6)	
C8	−0.4313 (3)	−0.3311 (3)	0.6305 (3)	0.0287 (10)	
H8A	−0.4052	−0.3920	0.6588	0.034*	
H8B	−0.4146	−0.2774	0.6759	0.034*	
C9	−0.5404 (3)	−0.3388 (3)	0.6225 (3)	0.0245 (9)	
C10	−0.6110 (3)	−0.2770 (3)	0.6542 (3)	0.0321 (9)	

H10	−0.6012	−0.2163	0.6859	0.038*	
C100	−0.0049 (4)	0.1275 (3)	0.1186 (3)	0.0557 (11)	
H10A	0.0377	0.1242	0.0608	0.084*	
H10B	−0.0637	0.0886	0.1069	0.084*	
H10C	0.0298	0.1021	0.1762	0.084*	
C11	−0.6796 (3)	−0.4027 (3)	0.5859 (3)	0.0272 (9)	
H11	−0.7281	−0.4455	0.5611	0.033*	
O11	−0.0318 (3)	0.2254 (2)	0.1361 (2)	0.0625 (10)	
H11A	−0.0627	0.2468	0.0873	0.094*	
C12	−0.4237 (3)	−0.0397 (2)	0.8098 (3)	0.0209 (8)	
C13	−0.4217 (3)	−0.0407 (3)	0.7086 (3)	0.0345 (10)	
H13	−0.3681	−0.0685	0.6744	0.041*	
C14	−0.5000	0.0000	0.6568 (4)	0.0493 (17)	
H14	−0.5000	0.0000	0.5869	0.059*	
C15	−0.3479 (3)	−0.0782 (2)	0.8793 (2)	0.0211 (8)	
C16	−0.2992 (3)	−0.0964 (2)	1.0444 (2)	0.0222 (8)	
H16	−0.2344	−0.0723	1.0209	0.027*	
C17	−0.2936 (3)	−0.2061 (3)	1.0588 (2)	0.0222 (8)	
C18	−0.1962 (3)	−0.3332 (2)	1.1250 (3)	0.0314 (9)	
H18A	−0.1270	−0.3454	1.1384	0.047*	
H18B	−0.2168	−0.3717	1.0680	0.047*	
H18C	−0.2351	−0.3516	1.1826	0.047*	
C19	−0.3216 (3)	−0.0500 (2)	1.1451 (3)	0.0251 (9)	
H19A	−0.3804	−0.0811	1.1734	0.030*	
H19B	−0.2663	−0.0624	1.1903	0.030*	
C20	−0.3383 (3)	0.0574 (2)	1.1379 (3)	0.0221 (8)	
C21	−0.2801 (3)	0.1340 (3)	1.1632 (2)	0.0264 (8)	
H21	−0.2175	0.1308	1.1933	0.032*	
C22	−0.4153 (3)	0.1889 (2)	1.0961 (3)	0.0243 (8)	
H22	−0.4629	0.2325	1.0709	0.029*	
O12	−0.5670 (9)	0.0368 (19)	0.4155 (9)	0.261 (12)	0.50
C201	−0.495 (3)	−0.022 (4)	0.3637 (9)	0.127 (15)	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0194 (3)	0.0192 (3)	0.0214 (3)	−0.0025 (3)	0.000	0.000
O1	0.0409 (18)	0.0325 (15)	0.0313 (15)	−0.0211 (14)	−0.0055 (13)	0.0061 (12)
N1	0.017 (2)	0.0204 (19)	0.0199 (17)	−0.001 (2)	0.000	0.000
C1	0.0170 (19)	0.0213 (19)	0.026 (2)	−0.0005 (16)	−0.0040 (15)	0.0020 (15)
N2	0.0215 (17)	0.0207 (15)	0.0247 (16)	−0.0046 (14)	−0.0053 (13)	0.0008 (12)
Cu2	0.0188 (3)	0.0179 (3)	0.0201 (3)	0.0005 (3)	0.000	0.000
C2	0.035 (2)	0.027 (2)	0.026 (2)	−0.0147 (18)	0.0011 (16)	0.0056 (16)
O2	0.0286 (17)	0.0528 (19)	0.064 (2)	−0.0093 (16)	−0.0049 (16)	0.0069 (16)
N3	0.028 (2)	0.0336 (18)	0.0291 (17)	0.0136 (16)	0.0041 (14)	−0.0031 (14)
O3	0.044 (2)	0.064 (2)	0.0369 (17)	−0.0329 (17)	−0.0093 (14)	−0.0055 (14)
C3	0.050 (4)	0.041 (3)	0.021 (2)	−0.018 (4)	0.000	0.000
N4	0.0218 (17)	0.0237 (16)	0.0252 (16)	0.0024 (15)	−0.0017 (13)	0.0004 (13)

C4	0.018 (2)	0.0220 (19)	0.030 (2)	−0.0034 (16)	−0.0042 (15)	0.0019 (15)
O4	0.0337 (17)	0.0282 (14)	0.0308 (15)	0.0126 (13)	0.0078 (12)	0.0063 (11)
N5	0.030 (2)	0.0125 (18)	0.0219 (18)	−0.003 (2)	0.000	0.000
O5	0.0285 (15)	0.0203 (13)	0.0374 (15)	−0.0036 (12)	−0.0031 (12)	0.0038 (11)
C5	0.033 (2)	0.027 (2)	0.030 (2)	−0.0073 (17)	−0.0115 (17)	−0.0001 (16)
O6	0.0273 (15)	0.0199 (13)	0.0371 (15)	0.0093 (12)	−0.0061 (12)	0.0008 (11)
C6	0.038 (3)	0.051 (3)	0.021 (2)	−0.017 (2)	−0.0098 (19)	0.0127 (19)
N6	0.0195 (15)	0.0163 (14)	0.0210 (15)	0.0040 (13)	0.0000 (12)	0.0002 (12)
N7	0.0271 (19)	0.0172 (16)	0.0299 (17)	−0.0066 (14)	−0.0002 (14)	−0.0019 (13)
C7	0.060 (4)	0.121 (5)	0.035 (3)	−0.061 (3)	−0.012 (2)	0.018 (3)
N8	0.0201 (16)	0.0144 (15)	0.0246 (16)	−0.0015 (13)	−0.0021 (13)	−0.0025 (12)
C8	0.030 (2)	0.030 (2)	0.026 (2)	−0.0027 (19)	−0.0106 (18)	−0.0069 (17)
C9	0.030 (2)	0.024 (2)	0.020 (2)	0.0057 (17)	0.0000 (16)	−0.0018 (15)
C10	0.040 (3)	0.027 (2)	0.028 (2)	0.004 (2)	−0.0044 (18)	−0.0081 (17)
C100	0.066 (3)	0.052 (3)	0.049 (2)	0.015 (3)	−0.002 (3)	−0.0067 (19)
C11	0.026 (2)	0.026 (2)	0.029 (2)	0.0058 (17)	−0.0020 (17)	−0.0001 (16)
O11	0.081 (3)	0.053 (2)	0.053 (2)	0.0131 (18)	−0.0121 (17)	−0.0071 (16)
C12	0.024 (2)	0.0166 (16)	0.0219 (18)	0.0038 (15)	0.0042 (16)	−0.0004 (13)
C13	0.048 (3)	0.035 (2)	0.021 (2)	0.016 (2)	0.0094 (18)	−0.0004 (15)
C14	0.064 (4)	0.064 (4)	0.020 (2)	0.034 (5)	0.000	0.000
C15	0.028 (2)	0.0104 (16)	0.0248 (19)	0.0004 (16)	0.0030 (15)	0.0030 (14)
C16	0.0180 (19)	0.0203 (18)	0.0283 (19)	0.0000 (16)	0.0024 (15)	0.0039 (15)
C17	0.025 (2)	0.0210 (19)	0.0205 (18)	0.0077 (18)	0.0083 (15)	0.0041 (14)
C18	0.039 (3)	0.0208 (19)	0.035 (2)	0.0124 (18)	−0.0047 (19)	0.0031 (16)
C19	0.027 (2)	0.024 (2)	0.024 (2)	−0.0003 (17)	−0.0014 (17)	−0.0001 (16)
C20	0.024 (2)	0.0163 (19)	0.026 (2)	−0.0053 (17)	0.0024 (16)	−0.0018 (16)
C21	0.020 (2)	0.033 (2)	0.027 (2)	−0.0047 (18)	−0.0005 (15)	−0.0049 (16)
C22	0.027 (2)	0.0196 (19)	0.026 (2)	0.0002 (17)	0.0006 (16)	−0.0015 (15)
O12	0.096 (9)	0.58 (4)	0.103 (9)	−0.084 (15)	0.006 (7)	−0.129 (16)
C201	0.100 (13)	0.23 (5)	0.057 (6)	−0.063 (16)	−0.032 (15)	0.020 (12)

Geometric parameters (Å, °)

Cu1—N1	1.937 (3)	N6—C16	1.456 (4)
Cu1—N2^{i}	2.020 (3)	N7—C22	1.347 (4)
Cu1—N2	2.020 (3)	N7—C21	1.383 (5)
Cu1—N4^{i}	2.071 (3)	N7—H7	0.8800
Cu1—N4	2.071 (3)	C7—H7A	0.9800
O1—C4	1.271 (4)	C7—H7B	0.9800
N1—C1	1.331 (4)	C7—H7C	0.9800
N1—C1^{i}	1.331 (4)	N8—C22	1.329 (4)
C1—C2	1.381 (5)	N8—C20	1.403 (4)
C1—C4	1.514 (5)	C8—C9	1.502 (5)
N2—C4	1.315 (4)	C8—H8A	0.9900
N2—C5	1.461 (4)	C8—H8B	0.9900
Cu2—N5	1.956 (3)	C9—C10	1.359 (5)
Cu2—N6	2.020 (3)	C10—H10	0.9500
Cu2—N6^{ii}	2.020 (3)	C100—O11	1.416 (5)

Cu2—N8	2.094 (3)	C100—H10A	0.9800
Cu2—N8^{ii}	2.094 (3)	C100—H10B	0.9800
C2—C3	1.390 (4)	C100—H10C	0.9800
C2—H2	0.9500	C11—H11	0.9500
O2—C6	1.194 (5)	O11—H11A	0.8400
N3—C11	1.342 (5)	C12—C13	1.376 (5)
N3—C10	1.369 (5)	C12—C15	1.500 (5)
N3—H3	0.8800	C13—C14	1.399 (5)
O3—C6	1.351 (5)	C13—H13	0.9500
O3—C7	1.459 (5)	C14—C13^{ii}	1.399 (5)
C3—C2^{i}	1.390 (4)	C14—H14	0.9500
C3—H3A	0.9500	C16—C17	1.525 (5)
N4—C11	1.328 (4)	C16—C19	1.541 (5)
N4—C9	1.383 (4)	C16—H16	1.0000
O4—C15	1.263 (4)	C18—H18A	0.9800
N5—C12	1.339 (4)	C18—H18B	0.9800
N5—C12^{ii}	1.339 (4)	C18—H18C	0.9800
O5—C17	1.213 (4)	C19—C20	1.499 (4)
C5—C6	1.520 (6)	C19—H19A	0.9900
C5—C8	1.556 (5)	C19—H19B	0.9900
C5—H5	1.0000	C20—C21	1.368 (5)
O6—C17	1.337 (4)	C21—H21	0.9500
O6—C18	1.456 (4)	C22—H22	0.9500
N6—C15	1.318 (4)	O12—C201	1.452 (10)
N1—Cu1—N2^{i}	79.45 (8)	H7B—C7—H7C	109.5
N1—Cu1—N2	79.45 (8)	C22—N8—C20	105.3 (3)
N2^{i}—Cu1—N2	158.89 (16)	C22—N8—Cu2	131.2 (2)
N1—Cu1—N4^{i}	129.05 (8)	C20—N8—Cu2	117.1 (2)
N2^{i}—Cu1—N4^{i}	89.80 (11)	C9—C8—C5	112.4 (3)
N2—Cu1—N4^{i}	103.55 (11)	C9—C8—H8A	109.1
N1—Cu1—N4	129.05 (8)	C5—C8—H8A	109.1
N2^{i}—Cu1—N4	103.55 (11)	C9—C8—H8B	109.1
N2—Cu1—N4	89.80 (11)	C5—C8—H8B	109.1
N4^{i}—Cu1—N4	101.91 (15)	H8A—C8—H8B	107.9
C1—N1—C1^{i}	122.5 (4)	C10—C9—N4	108.8 (3)
C1—N1—Cu1	118.75 (19)	C10—C9—C8	129.9 (4)
C1^{i}—N1—Cu1	118.75 (19)	N4—C9—C8	121.2 (3)
N1—C1—C2	120.4 (3)	C9—C10—N3	107.2 (3)
N1—C1—C4	112.6 (3)	C9—C10—H10	126.4
C2—C1—C4	127.0 (3)	N3—C10—H10	126.4
C4—N2—C5	116.5 (3)	O11—C100—H10A	109.5
C4—N2—Cu1	116.6 (2)	O11—C100—H10B	109.5
C5—N2—Cu1	126.0 (2)	H10A—C100—H10B	109.5
N5—Cu2—N6	79.23 (8)	O11—C100—H10C	109.5
N5—Cu2—N6^{ii}	79.23 (8)	H10A—C100—H10C	109.5
N6—Cu2—N6^{ii}	158.45 (15)	H10B—C100—H10C	109.5

N5—Cu2—N8	128.27 (8)	N4—C11—N3	111.6 (3)
N6—Cu2—N8	89.18 (11)	N4—C11—H11	124.2
N6^{ii}—Cu2—N8	104.23 (10)	N3—C11—H11	124.2
N5—Cu2—N8^{ii}	128.27 (8)	C100—O11—H11A	109.5
N6—Cu2—N8^{ii}	104.23 (10)	N5—C12—C13	119.4 (3)
N6^{ii}—Cu2—N8^{ii}	89.18 (11)	N5—C12—C15	112.8 (3)
N8—Cu2—N8^{ii}	103.46 (15)	C13—C12—C15	127.8 (3)
C1—C2—C3	118.0 (3)	C12—C13—C14	118.9 (4)
C1—C2—H2	121.0	C12—C13—H13	120.5
C3—C2—H2	121.0	C14—C13—H13	120.5
C11—N3—C10	106.9 (3)	C13—C14—C13^{ii}	119.7 (5)
C11—N3—H3	126.6	C13—C14—H14	120.2
C10—N3—H3	126.6	C13^{ii}—C14—H14	120.2
C6—O3—C7	115.5 (4)	O4—C15—N6	127.6 (3)
C2^{i}—C3—C2	120.6 (4)	O4—C15—C12	119.3 (3)
C2^{i}—C3—H3A	119.7	N6—C15—C12	113.0 (3)
C2—C3—H3A	119.7	N6—C16—C17	111.5 (3)
C11—N4—C9	105.5 (3)	N6—C16—C19	110.8 (3)
C11—N4—Cu1	132.8 (2)	C17—C16—C19	107.9 (3)
C9—N4—Cu1	117.1 (2)	N6—C16—H16	108.9
O1—C4—N2	129.3 (3)	C17—C16—H16	108.9
O1—C4—C1	118.3 (3)	C19—C16—H16	108.9
N2—C4—C1	112.5 (3)	O5—C17—O6	124.0 (3)
C12—N5—C12^{ii}	123.6 (4)	O5—C17—C16	125.4 (3)
C12—N5—Cu2	118.2 (2)	O6—C17—C16	110.6 (3)
C12^{ii}—N5—Cu2	118.2 (2)	O6—C18—H18A	109.5
N2—C5—C6	112.1 (3)	O6—C18—H18B	109.5
N2—C5—C8	110.5 (3)	H18A—C18—H18B	109.5
C6—C5—C8	107.3 (3)	O6—C18—H18C	109.5
N2—C5—H5	109.0	H18A—C18—H18C	109.5
C6—C5—H5	109.0	H18B—C18—H18C	109.5
C8—C5—H5	109.0	C20—C19—C16	112.4 (4)
C17—O6—C18	116.7 (3)	C20—C19—H19A	109.1
O2—C6—O3	124.6 (4)	C16—C19—H19A	109.1
O2—C6—C5	126.6 (4)	C20—C19—H19B	109.1
O3—C6—C5	108.8 (4)	C16—C19—H19B	109.1
C15—N6—C16	116.0 (3)	H19A—C19—H19B	107.9
C15—N6—Cu2	116.6 (2)	C21—C20—N8	109.0 (3)
C16—N6—Cu2	126.3 (2)	C21—C20—C19	130.9 (4)
C22—N7—C21	107.4 (3)	N8—C20—C19	120.0 (3)
C22—N7—H7	126.3	C20—C21—N7	106.4 (3)
C21—N7—H7	126.3	C20—C21—H21	126.8
O3—C7—H7A	109.5	N7—C21—H21	126.8
O3—C7—H7B	109.5	N8—C22—N7	111.9 (3)
H7A—C7—H7B	109.5	N8—C22—H22	124.1
O3—C7—H7C	109.5	N7—C22—H22	124.1
H7A—C7—H7C	109.5		

N2^{i}—Cu1—N1—C1	179.10 (19)	N8—Cu2—N6—C16	41.8 (3)
N2—Cu1—N1—C1	−0.90 (19)	N8^{ii}—Cu2—N6—C16	−61.9 (3)
N4^{i}—Cu1—N1—C1	−99.9 (2)	N5—Cu2—N8—C22	46.9 (3)
N4—Cu1—N1—C1	80.1 (2)	N6—Cu2—N8—C22	122.4 (3)
N2^{i}—Cu1—N1—C1^{i}	−0.90 (19)	N6^{ii}—Cu2—N8—C22	−40.5 (3)
N2—Cu1—N1—C1^{i}	179.10 (19)	N8^{ii}—Cu2—N8—C22	−133.1 (3)
N4^{i}—Cu1—N1—C1^{i}	80.1 (2)	N5—Cu2—N8—C20	−100.4 (2)
N4—Cu1—N1—C1^{i}	−99.9 (2)	N6—Cu2—N8—C20	−24.9 (2)
C1^{i}—N1—C1—C2	0.4 (3)	N6^{ii}—Cu2—N8—C20	172.2 (2)
Cu1—N1—C1—C2	−179.6 (3)	N8^{ii}—Cu2—N8—C20	79.6 (2)
C1^{i}—N1—C1—C4	178.7 (3)	N2—C5—C8—C9	−50.4 (4)
Cu1—N1—C1—C4	−1.3 (3)	C6—C5—C8—C9	−172.9 (3)
N1—Cu1—N2—C4	3.3 (2)	C11—N4—C9—C10	0.2 (4)
N2^{i}—Cu1—N2—C4	3.3 (2)	Cu1—N4—C9—C10	159.3 (2)
N4^{i}—Cu1—N2—C4	131.2 (2)	C11—N4—C9—C8	179.0 (4)
N4—Cu1—N2—C4	−126.6 (3)	Cu1—N4—C9—C8	−21.8 (5)
N1—Cu1—N2—C5	171.8 (3)	C5—C8—C9—C10	−110.0 (5)
N2^{i}—Cu1—N2—C5	171.8 (3)	C5—C8—C9—N4	71.4 (5)
N4^{i}—Cu1—N2—C5	−60.3 (3)	N4—C9—C10—N3	0.6 (4)
N4—Cu1—N2—C5	41.9 (3)	C8—C9—C10—N3	−178.1 (4)
N1—C1—C2—C3	−0.8 (5)	C11—N3—C10—C9	−1.2 (4)
C4—C1—C2—C3	−178.8 (3)	C9—N4—C11—N3	−1.0 (4)
C1—C2—C3—C2^{i}	0.4 (2)	Cu1—N4—C11—N3	−155.4 (3)
N1—Cu1—N4—C11	50.6 (4)	C10—N3—C11—N4	1.4 (4)
N2^{i}—Cu1—N4—C11	−36.7 (3)	C12^{ii}—N5—C12—C13	0.0 (2)
N2—Cu1—N4—C11	126.8 (3)	Cu2—N5—C12—C13	−180.0 (2)
N4^{i}—Cu1—N4—C11	−129.4 (4)	C12^{ii}—N5—C12—C15	179.5 (3)
N1—Cu1—N4—C9	−101.4 (2)	Cu2—N5—C12—C15	−0.5 (3)
N2^{i}—Cu1—N4—C9	171.3 (2)	N5—C12—C13—C14	0.0 (5)
N2—Cu1—N4—C9	−25.2 (2)	C15—C12—C13—C14	−179.5 (3)
N4^{i}—Cu1—N4—C9	78.6 (2)	C12—C13—C14—C13^{ii}	0.0 (2)
C5—N2—C4—O1	3.9 (5)	C16—N6—C15—O4	4.6 (5)
Cu1—N2—C4—O1	173.5 (3)	Cu2—N6—C15—O4	173.3 (3)
C5—N2—C4—C1	−174.4 (3)	C16—N6—C15—C12	−173.6 (3)
Cu1—N2—C4—C1	−4.8 (4)	Cu2—N6—C15—C12	−4.8 (4)
N1—C1—C4—O1	−174.6 (3)	N5—C12—C15—O4	−174.9 (3)
C2—C1—C4—O1	3.6 (5)	C13—C12—C15—O4	4.6 (5)
N1—C1—C4—N2	3.9 (4)	N5—C12—C15—N6	3.5 (4)
C2—C1—C4—N2	−177.9 (4)	C13—C12—C15—N6	−177.1 (3)
N6—Cu2—N5—C12	−1.58 (18)	C15—N6—C16—C17	−80.8 (4)
N6^{ii}—Cu2—N5—C12	178.42 (18)	Cu2—N6—C16—C17	111.7 (3)
N8—Cu2—N5—C12	78.72 (19)	C15—N6—C16—C19	159.0 (3)
N8^{ii}—Cu2—N5—C12	−101.28 (19)	Cu2—N6—C16—C19	−8.5 (4)
N6—Cu2—N5—C12^{ii}	178.42 (18)	C18—O6—C17—O5	−0.2 (5)

N6^{ii}—Cu2—N5—C12^{ii}	−1.58 (18)	C18—O6—C17—C16	178.6 (3)
N8—Cu2—N5—C12^{ii}	−101.28 (19)	N6—C16—C17—O5	−17.1 (5)
N8^{ii}—Cu2—N5—C12^{ii}	78.72 (19)	C19—C16—C17—O5	104.7 (4)
C4—N2—C5—C6	−80.7 (4)	N6—C16—C17—O6	164.1 (3)
Cu1—N2—C5—C6	110.7 (3)	C19—C16—C17—O6	−74.1 (4)
C4—N2—C5—C8	159.7 (3)	N6—C16—C19—C20	−52.2 (4)
Cu1—N2—C5—C8	−8.8 (4)	C17—C16—C19—C20	−174.5 (3)
C7—O3—C6—O2	1.6 (6)	C22—N8—C20—C21	0.6 (4)
C7—O3—C6—C5	179.9 (3)	Cu2—N8—C20—C21	155.7 (2)
N2—C5—C6—O2	−12.9 (6)	C22—N8—C20—C19	−177.2 (4)
C8—C5—C6—O2	108.6 (4)	Cu2—N8—C20—C19	−22.2 (5)
N2—C5—C6—O3	168.9 (3)	C16—C19—C20—C21	−104.8 (5)
C8—C5—C6—O3	−69.6 (4)	C16—C19—C20—N8	72.5 (5)
N5—Cu2—N6—C15	3.7 (2)	N8—C20—C21—N7	−0.2 (4)
N6^{ii}—Cu2—N6—C15	3.7 (2)	C19—C20—C21—N7	177.3 (4)
N8—Cu2—N6—C15	−125.6 (2)	C22—N7—C21—C20	−0.3 (4)
N8^{ii}—Cu2—N6—C15	130.7 (2)	C20—N8—C22—N7	−0.8 (4)
N5—Cu2—N6—C16	171.1 (3)	Cu2—N8—C22—N7	−150.9 (3)
N6^{ii}—Cu2—N6—C16	171.1 (3)	C21—N7—C22—N8	0.7 (4)

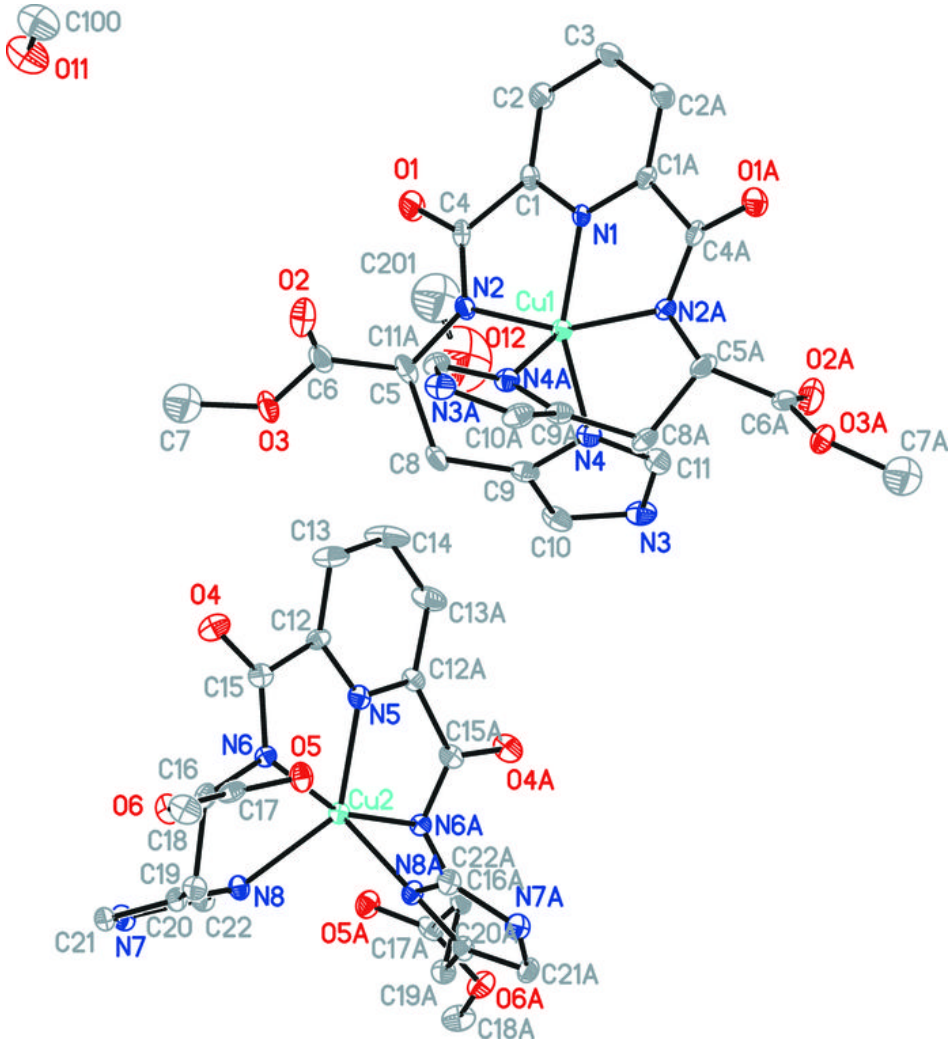
Symmetry codes: (i) −*x*−1, −*y*−1, *z*; (ii) −*x*−1, −*y*, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{iii}	0.88	1.86	2.719 (4)	166
N7—H7···O4^{iv}	0.88	1.88	2.738 (4)	163
O11—H11A···O5^{v}	0.84	2.00	2.785 (4)	155

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

Fig. 1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C17A
C20A
C21A
C19A
O6A
C18A