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Synthesis, crystal structure and Hirshfeld surface analysis of $[Cu(NO_3)_2\{8\text{-methylphenanthridin-}6(5H)\text{-one}\}_4]$

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Keywords: copper complexes; N-containing compounds; crystal structure; non-covalent interactions.

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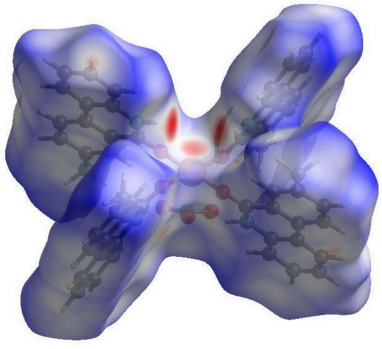
The asymmetric unit of the title compound, tetrakis[8-methylphenanthridin-6(5*H*)-one-κO]bis(nitrato-κO)copper(II), $[Cu(NO_3)_2(C_{14}H_{11}NO)_4]$, contains one Cu^{II} cation located on a centre of symmetry, two 8-methylphenanthridin-6(5*H*)-one (MPHNT) ligands and one nitrate anion, where the Cu^{II} atom is in a slightly distorted octahedral environment. Intramolecular N—H···O hydrogen bonds are observed. In the crystal, C—H···O hydrogen bonds link the molecules, enclosing S(6), S(9) and $R_4^4(18)$ ring motifs. In addition π–π interactions with centroid-to-centroid distances of 3.808 (2) Å and also a series of C—H···π(ring) interactions help to consolidate the packing in a three-dimensional architecture within the crystal. A Hirshfeld surface analysis revealed that the most important contributions for the crystal packing are from H···H (41.1%), H···C/C···H (29.9%), H···O/O···H (14.8%) and C···C (10.0%) interactions.

1. Chemical context

N-containing organic compounds are a widely used and versatile class of ligands in coordination chemistry due to the nitrogen atom's strong σ-donor characteristics, which stabilize various metal oxidation states (Gurbanov *et al.*, 2023; Mahmudov *et al.*, 2021, 2023; Kretschmer, 2020; Peris, 2018). These ligands are employed in diverse applications, including molecular recognition, homogenous catalysis, crystal engineering, material science, organic synthesis and medicinal chemistry (Gadzhieva *et al.*, 2005; Maharramov *et al.*, 2011; Gurbanov *et al.*, 2022). Alteration of the metal centre as well as substituents at the N-ligands dictate the sensing and analytical properties, catalytic activity, and supramolecular arrangements of the corresponding metal complexes (Aliyeva *et al.*, 2024; Gurbanov *et al.*, 2018; Huseynov *et al.*, 2018). In particular, the coordination chemistry of copper with N-ligands is extremely rich due to its oxidation states Cu^0, Cu^I, Cu^{II} and Cu^{III} allowing it to act through one- or two-electron processes in organic transformations (Allen *et al.*, 2013). We have synthesized a new copper(II) complex with an 8-methylphenanthridin-6(5*H*)-one ligand, which is consolidated through intra- and intermolecular non-covalent interactions. Herein, we report its synthesis and molecular and crystal structures together with the results of a Hirshfeld surface analysis.



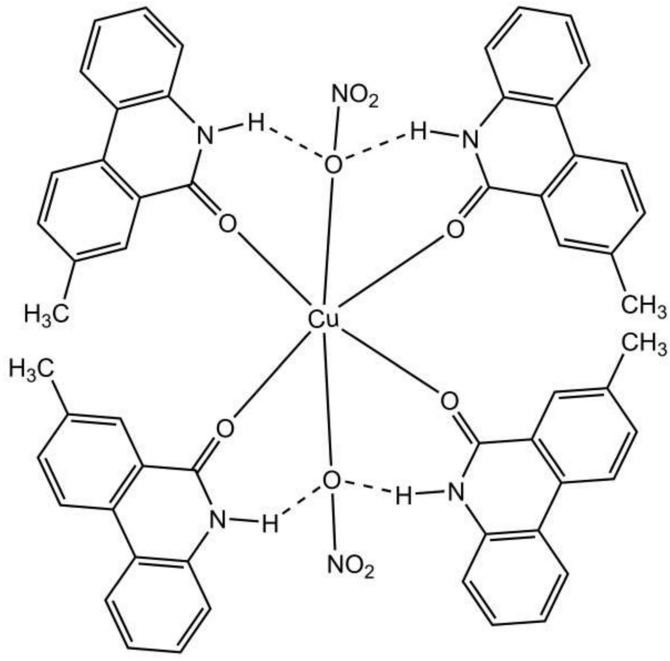


Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.942 (2)	Cu1—O5	2.520 (3)
Cu1—O1	1.953 (2)		
O2^{ii}—Cu1—O1	90.74 (11)	O1—Cu1—O5	90.79 (11)
O2—Cu1—O1	89.26 (11)	O2—Cu1—O5	94.21 (11)

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

2. Structural commentary

The asymmetric unit of the title compound, $C_{56}H_{44}CuN_6O_{10}$, (I) contains one Cu^{II} cation located on a crystallographic inversion centre, two 8-methylphenanthridin-6(5*H*)-one (MPHNT) and one nitrate anion (Fig. 1). The Cu^{II} atom is in a slightly distorted octahedral environment and is coordinated by four symmetry-related MPHNT O atoms (O1, O2 and O1′, O2′) in the basal plane at distances of 1.953 (2) and 1.942 (2) Å in a square-planar arrangement and by two symmetry-related O atoms (O5 and O5′>) at distances of 2.520 (3) Å in the axial positions (Table 1) [symmetry code: (′) $\frac{1}{2}-x, \frac{1}{2}-y, -z+1$]. The phenanthridin ring systems [(*A* (N1/C1–C13) and (*B* (N2/C15–C27)] are essentially planar with r.m.s. deviations of 0.03 (4) and 0.03 (6) Å, respectively (Fig. 1). Atoms O1, O2, C14 and C28 are −0.006 (3), 0.182 (3), 0.046 (6) and 0.100 (6) Å away from the best least-squares planes of the corresponding ring systems. The ring systems are oriented at a dihedral angle of *A*/*B* = 68.97 (6)°. Intramolecular N—H···O hydrogen bonds (Table 2) occur between N atoms of MPHNT and O atoms of nitrate anions (Fig. 1).

3. Supramolecular features

In the crystal, C—H···O hydrogen bonds (Table 2) link the molecules, enclosing $S(6)$, $S(9)$ and $R_4^4(18)$ ring motifs (Etter *et al.*, 1990) (Fig. 2). In addition, π–π interactions between (N2/C15/C16/C21/C22/C27) and (C22–C27) rings with centroid–to–centroid distances of 3.808 (2) Å [where α = 0.8 (2)° and slippage = 1.592 Å] and a series of the C—H···π(ring) interactions (Table 2) help to consolidate the packing in a three-dimensional architecture within the crystal.

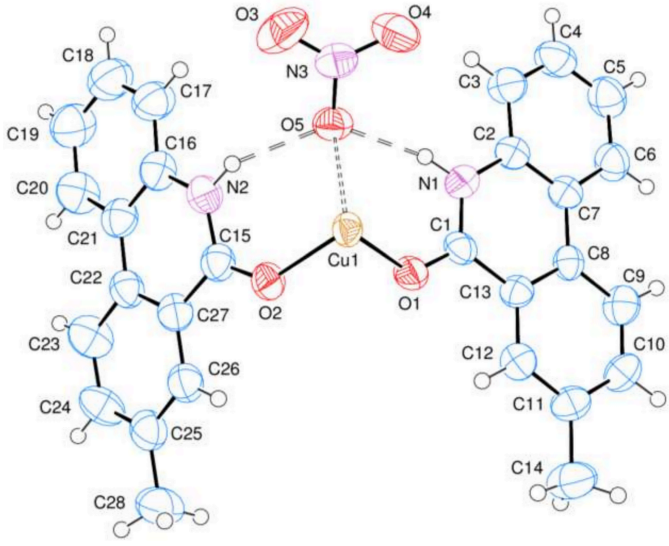


Figure 1
The asymmetric unit of the title compound with the atom-numbering scheme and 50% probability ellipsoids. Intramolecular N—H···O hydrogen bonds are shown as dashed lines.

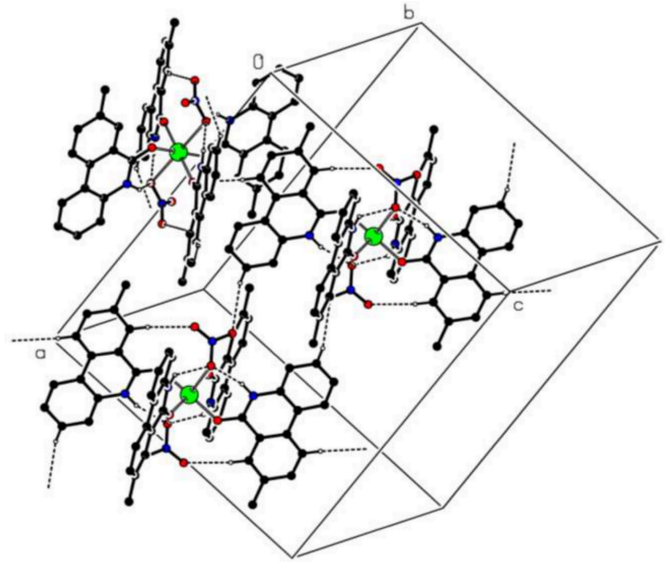


Figure 2
The partial packing diagram of the title compound. Intramolecular N—H···O and intermolecular C—H···O hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions been omitted for clarity.

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

*Cg*1, *Cg*3, *Cg*4 and *Cg*5 are the centroids of the (N1/C1/C2/C7/C8/C13), (C2–C7), (C8–C13) and (C16–C21) rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O5	0.90	1.97	2.852 (4)	165
N2—H2*N*···O5	0.90	2.07	2.806 (4)	139
C4—H4*A*···O4^{iii}	0.93	2.60	3.433 (6)	150
C9—H9*A*···O1^{i}	0.93	2.60	3.514 (5)	169
C12—H12*A*···O3^{ii}	0.93	2.57	3.455 (6)	158
C14—H14*C*···*Cg*5^{vi}	0.96	2.92	3.768 (6)	147
C20—H20*A*···*Cg*3^{vii}	0.93	2.86	3.644 (5)	143
C23—H23*A*···*Cg*1^{vii}	0.93	2.89	3.726 (5)	151
C24—H24*A*···*Cg*4^{vii}	0.93	2.77	3.557 (5)	143
C28—H28*C*···*Cg*3^{viii}	0.96	2.88	3.716 (6)	146

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

4. Hirshfeld surface analysis

To visualize the intermolecular interactions in the title compound, a Hirshfeld surface (HS) analysis was carried out using *Crystal Explorer 17.5* (Spackman *et al.*, 2021). In the HS plotted over d_{norm} (Fig. 3), the contact distances equal, shorter and longer than the sum of van der Waals radii are shown by the white, red and blue colours, respectively. According to the two-dimensional fingerprint plots, H···H, H···C/C···H, H···O/O···H and C···C contacts make the most important contributions to the HS (Fig. 4).

5. Synthesis and crystallization

832 mg (4.0 mmol) of 8-methylphenanthridin-6(5H)-one were dissolved in 100 mL of ethanol and 233 mg (1.0 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ were added with stirring. The mixture was stirred for 5 min and left standing for slow solvent evaporation. Brown crystals started to form in the reaction mixture after 2 d at room temperature. After 3 d they were filtered off and dried in air. Yield: 55% (based on Cu). Analysis calculated for $C_{56}H_{44}CuN_6O_{10}$ (M = 1024.55): C, 65.65; H, 4.33; N, 8.20. Found: C 65.62; H, 4.30; N, 8.17%. IR, cm^{-1}: 3212 ν(N—H) and 1648 ν(C═O).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu(NO_3)_2(C_{14}H_{11}NO)_4]$
M_r	1024.51
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	22.279 (2), 11.9230 (11), 18.1267 (16)
β (°)	102.444 (4)
V (Å^3)	4701.9 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.54
Crystal size (mm)	0.26 × 0.21 × 0.11
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.861, 0.934
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31022, 4623, 2755
R_{int}	0.087
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.184, 1.02
No. of reflections	4623
No. of parameters	333
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.64, −0.28

Computer programs: *APEX4* and *SAINT* (Bruker, 2016), *SHELXT2019/1* (Sheldrick, 2015*a*), *SHELXL2019/1* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* and *WinGX* publication routines (Farrugia, 2012) and *PLATON* (Spek, 2020).

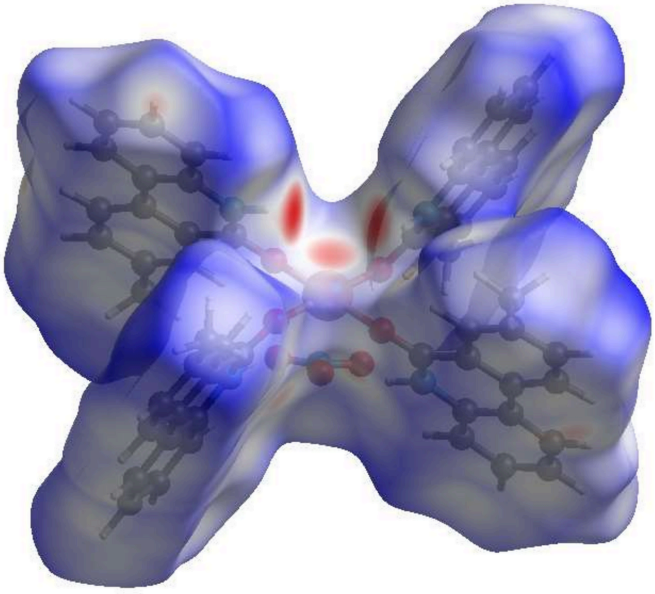


Figure 3
View of the three-dimensional Hirshfeld surface plotted over d_{norm}.

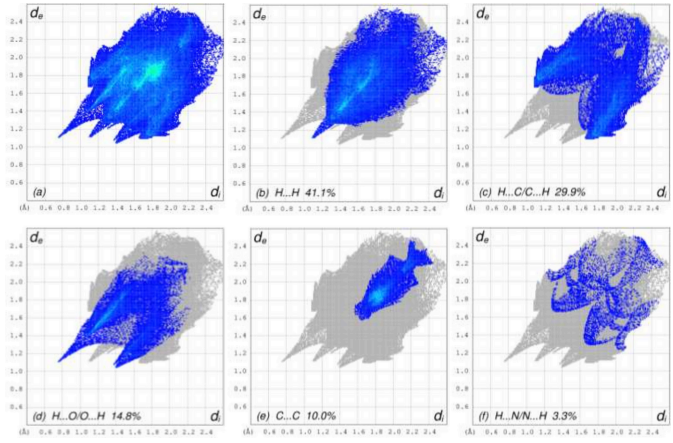


Figure 4
The full two-dimensional fingerprint plots, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) H···C/C···H, (*d*) H···O/O···H, (*e*) C···C, (*f*) H···N/N···H, (*g*) C···N/N···C, (*h*) O···O, (*i*) O···Cu/Cu···O and (*j*) N···O/O···N interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The N- and C-bound H-atom positions were calculated geometrically at distances of 0.90 (for NH), 0.93 (for aromatic CH) and 0.96 Å (for CH_3) and refined using a riding model by applying the constraint of $U_{iso}(H) = k \times U_{eq}(C,N)$, where $k = 1.5$ for methyl H atoms and k = 1.2 for the other H atoms.

Acknowledgements

The authors' contributions are as follows. Conceptualization, AVG, TH and MMW; synthesis and X-ray analysis AVG; Hirshfeld surface analysis, TH; funding acquisition, AVG; writing (review and editing of the manuscript), AVG and TH; supervision, TH.

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supporting information

Acta Cryst. (2025). E**81**, 1140-1143 [https://doi.org/10.1107/S2056989025009892]

Synthesis, crystal structure and Hirshfeld surface analysis of $[Cu(NO_3)_2\{8\text{-methylphenanthridin-6(5}H\text{)-one}\}_4]$

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Computing details

Tetrakis[8-methylphenanthridin-6(5*H*)-one-κ*O*]bis(nitrato-κ*O*)copper(II)

Crystal data

$[Cu(NO_3)_2(C_{14}H_{11}NO)_4]$
M_r = 1024.51
Monoclinic, *C*2/*c*
a = 22.279 (2) Å
b = 11.9230 (11) Å
c = 18.1267 (16) Å
β = 102.444 (4)°
V = 4701.9 (8) Å^3
Z = 4
F(000) = 2124
D_x = 1.447 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3386 reflections
θ = 3.2–20.3°
μ = 0.54 mm^{-1}
T = 296 K
Prism, brown
0.26 × 0.21 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.861, T_{max} = 0.934
31022 measured reflections
4623 independent reflections
2755 reflections with $I > 2\sigma(I)$
R_{int} = 0.087
θ_{max} = 26.0°, θ_{min} = 3.2°
h = −27→27
k = −14→14
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.184
S = 1.02
4623 reflections
333 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0967P)^2 + 2.2853P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.250000	0.250000	0.500000	0.0399 (2)
O1	0.23229 (12)	0.2038 (2)	0.39416 (14)	0.0487 (7)
O2	0.23037 (12)	0.4036 (2)	0.46793 (15)	0.0490 (7)
O3	0.42140 (18)	0.2859 (4)	0.6104 (2)	0.0918 (12)
O4	0.41796 (16)	0.1304 (3)	0.5488 (2)	0.0909 (12)
O5	0.36260 (13)	0.2693 (2)	0.49965 (16)	0.0557 (8)
N1	0.31896 (15)	0.1148 (3)	0.38002 (19)	0.0510 (9)
H1N	0.339116	0.157220	0.418564	0.061*
N2	0.32132 (17)	0.4913 (3)	0.5025 (2)	0.0593 (10)
H2N	0.335582	0.427329	0.526291	0.071*
N3	0.40159 (17)	0.2283 (3)	0.5554 (2)	0.0583 (10)
C1	0.25888 (18)	0.1347 (3)	0.3591 (2)	0.0440 (9)
C2	0.35192 (18)	0.0411 (3)	0.3432 (2)	0.0470 (10)
C3	0.4148 (2)	0.0288 (4)	0.3704 (3)	0.0627 (12)
H3A	0.434875	0.069264	0.412391	0.075*
C4	0.4475 (2)	−0.0448 (4)	0.3342 (3)	0.0687 (13)
H4A	0.489718	−0.052775	0.351440	0.082*
C5	0.4174 (2)	−0.1058 (4)	0.2727 (3)	0.0694 (13)
H5A	0.439192	−0.155812	0.249106	0.083*
C6	0.3553 (2)	−0.0929 (4)	0.2464 (3)	0.0593 (12)
H6A	0.335682	−0.134016	0.204511	0.071*
C7	0.32065 (18)	−0.0194 (3)	0.2808 (2)	0.0475 (10)
C8	0.25515 (18)	−0.0035 (3)	0.2560 (2)	0.0437 (9)
C9	0.2184 (2)	−0.0650 (4)	0.1974 (2)	0.0587 (12)
H9A	0.236506	−0.119799	0.172896	0.070*
C10	0.1568 (2)	−0.0466 (4)	0.1753 (2)	0.0590 (11)
H10A	0.134131	−0.087837	0.135259	0.071*
C11	0.1266 (2)	0.0326 (4)	0.2113 (2)	0.0556 (11)
C12	0.16139 (19)	0.0903 (3)	0.2707 (2)	0.0499 (10)
H12A	0.142317	0.141936	0.296581	0.060*
C13	0.22473 (18)	0.0737 (3)	0.2935 (2)	0.0443 (9)
C14	0.0588 (2)	0.0528 (5)	0.1853 (3)	0.0811 (15)
H14A	0.044342	0.095921	0.222726	0.122*
H14B	0.037661	−0.017822	0.178320	0.122*
H14C	0.051105	0.093187	0.138434	0.122*
C15	0.2617 (2)	0.4901 (3)	0.4683 (2)	0.0508 (10)
C16	0.3621 (2)	0.5793 (4)	0.4979 (2)	0.0570 (11)
C17	0.4239 (2)	0.5659 (4)	0.5316 (3)	0.0736 (14)
H17A	0.437657	0.500156	0.557358	0.088*

C18	0.4649 (3)	0.6521 (5)	0.5264 (3)	0.0861 (16)
H18A	0.506435	0.644243	0.548237	0.103*
C19	0.4429 (3)	0.7502 (5)	0.4883 (3)	0.0865 (16)
H19A	0.469955	0.808523	0.484932	0.104*
C20	0.3808 (3)	0.7613 (4)	0.4551 (3)	0.0711 (14)
H20A	0.367097	0.827183	0.429407	0.085*
C21	0.3388 (2)	0.6769 (4)	0.4592 (2)	0.0592 (11)
C22	0.2743 (2)	0.6844 (3)	0.4257 (2)	0.0551 (11)
C23	0.2475 (3)	0.7787 (4)	0.3877 (3)	0.0724 (14)
H23A	0.271265	0.842018	0.384730	0.087*
C24	0.1844 (3)	0.7790 (4)	0.3534 (3)	0.0712 (14)
H24A	0.167386	0.842725	0.327463	0.085*
C25	0.1475 (2)	0.6888 (4)	0.3572 (3)	0.0652 (13)
C26	0.1735 (2)	0.5943 (4)	0.3975 (2)	0.0576 (11)
H26A	0.148801	0.532905	0.401998	0.069*
C27	0.2356 (2)	0.5913 (3)	0.4307 (2)	0.0525 (10)
C28	0.0813 (2)	0.6927 (5)	0.3189 (3)	0.0905 (17)
H28A	0.068979	0.769309	0.308519	0.136*
H28B	0.057088	0.659934	0.351196	0.136*
H28C	0.075071	0.651528	0.272393	0.136*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0504 (4)	0.0317 (3)	0.0358 (4)	−0.0007 (3)	0.0054 (3)	0.0007 (3)
O1	0.0540 (17)	0.0476 (14)	0.0409 (15)	0.0093 (14)	0.0027 (13)	−0.0027 (13)
O2	0.0569 (17)	0.0347 (14)	0.0542 (16)	−0.0018 (13)	0.0092 (14)	0.0065 (12)
O3	0.081 (3)	0.127 (3)	0.060 (2)	−0.011 (2)	−0.0015 (19)	−0.025 (2)
O4	0.068 (2)	0.073 (2)	0.122 (3)	0.0179 (19)	−0.002 (2)	0.013 (2)
O5	0.0504 (18)	0.0598 (18)	0.0530 (17)	0.0034 (14)	0.0028 (14)	0.0067 (13)
N1	0.048 (2)	0.053 (2)	0.049 (2)	−0.0009 (16)	0.0032 (17)	−0.0049 (16)
N2	0.064 (3)	0.0394 (19)	0.070 (2)	−0.0005 (17)	0.004 (2)	0.0080 (17)
N3	0.043 (2)	0.070 (3)	0.061 (2)	−0.0010 (19)	0.0082 (19)	0.0013 (19)
C1	0.050 (3)	0.039 (2)	0.041 (2)	0.0074 (18)	0.0065 (19)	0.0061 (17)
C2	0.046 (2)	0.048 (2)	0.048 (2)	0.0030 (19)	0.012 (2)	0.0027 (18)
C3	0.056 (3)	0.066 (3)	0.064 (3)	0.000 (2)	0.007 (2)	0.001 (2)
C4	0.051 (3)	0.072 (3)	0.085 (4)	0.009 (2)	0.018 (3)	0.008 (3)
C5	0.067 (3)	0.065 (3)	0.081 (3)	0.006 (3)	0.027 (3)	−0.004 (3)
C6	0.061 (3)	0.055 (3)	0.065 (3)	0.004 (2)	0.020 (2)	−0.009 (2)
C7	0.049 (3)	0.049 (2)	0.046 (2)	0.0028 (19)	0.012 (2)	0.0031 (18)
C8	0.052 (2)	0.040 (2)	0.040 (2)	−0.0011 (18)	0.0122 (18)	−0.0007 (16)
C9	0.069 (3)	0.064 (3)	0.044 (2)	−0.001 (2)	0.014 (2)	−0.009 (2)
C10	0.062 (3)	0.067 (3)	0.045 (2)	−0.011 (2)	0.005 (2)	−0.011 (2)
C11	0.053 (3)	0.067 (3)	0.044 (2)	−0.002 (2)	0.003 (2)	0.001 (2)
C12	0.056 (3)	0.053 (2)	0.042 (2)	0.001 (2)	0.014 (2)	−0.0004 (18)
C13	0.047 (2)	0.046 (2)	0.038 (2)	0.0000 (18)	0.0057 (18)	0.0031 (17)
C14	0.055 (3)	0.109 (4)	0.073 (3)	0.002 (3)	0.001 (3)	−0.010 (3)
C15	0.060 (3)	0.045 (2)	0.047 (2)	−0.001 (2)	0.009 (2)	0.0006 (19)

C16	0.067 (3)	0.052 (3)	0.052 (3)	−0.005 (2)	0.013 (2)	0.002 (2)
C17	0.067 (3)	0.069 (3)	0.079 (4)	−0.009 (3)	0.002 (3)	0.008 (3)
C18	0.074 (4)	0.088 (4)	0.091 (4)	−0.011 (3)	0.006 (3)	−0.002 (3)
C19	0.084 (4)	0.080 (4)	0.093 (4)	−0.013 (3)	0.013 (3)	0.010 (3)
C20	0.077 (4)	0.062 (3)	0.077 (3)	−0.004 (3)	0.023 (3)	0.021 (2)
C21	0.068 (3)	0.058 (3)	0.051 (2)	−0.002 (2)	0.011 (2)	−0.001 (2)
C22	0.067 (3)	0.048 (3)	0.051 (2)	0.005 (2)	0.012 (2)	0.0020 (19)
C23	0.080 (4)	0.064 (3)	0.077 (3)	0.004 (3)	0.025 (3)	0.025 (3)
C24	0.076 (4)	0.062 (3)	0.077 (3)	0.021 (3)	0.020 (3)	0.029 (3)
C25	0.077 (3)	0.062 (3)	0.054 (3)	0.012 (3)	0.008 (2)	−0.004 (2)
C26	0.064 (3)	0.049 (2)	0.059 (3)	0.003 (2)	0.012 (2)	−0.001 (2)
C27	0.062 (3)	0.049 (2)	0.045 (2)	0.003 (2)	0.010 (2)	0.0021 (19)
C28	0.074 (4)	0.101 (4)	0.087 (4)	0.029 (3)	−0.004 (3)	−0.003 (3)

Geometric parameters (Å, º)

Cu1—O2^{i}	1.942 (2)	C10—H10A	0.9300
Cu1—O2	1.942 (2)	C11—C12	1.369 (6)
Cu1—O1	1.953 (2)	C11—C14	1.502 (6)
Cu1—O5	2.520 (3)	C12—C13	1.396 (5)
Cu1—O1^{i}	1.953 (2)	C12—H12A	0.9300
O1—C1	1.264 (4)	C14—H14A	0.9600
O2—C15	1.245 (5)	C14—H14B	0.9600
O3—N3	1.212 (5)	C14—H14C	0.9600
O4—N3	1.237 (5)	C15—C27	1.446 (6)
O5—N3	1.279 (5)	C16—C17	1.390 (6)
N1—C1	1.331 (5)	C16—C21	1.400 (6)
N1—C2	1.403 (5)	C17—C18	1.391 (7)
N1—H1N	0.9000	C17—H17A	0.9300
N2—C15	1.339 (5)	C18—C19	1.393 (7)
N2—C16	1.401 (5)	C18—H18A	0.9300
N2—H2N	0.9001	C19—C20	1.392 (8)
C1—C13	1.460 (5)	C19—H19A	0.9300
C2—C3	1.389 (6)	C20—C21	1.388 (6)
C2—C7	1.394 (6)	C20—H20A	0.9300
C3—C4	1.392 (6)	C21—C22	1.437 (6)
C3—H3A	0.9300	C22—C23	1.385 (6)
C4—C5	1.377 (7)	C22—C27	1.420 (6)
C4—H4A	0.9300	C23—C24	1.409 (7)
C5—C6	1.371 (6)	C23—H23A	0.9300
C5—H5A	0.9300	C24—C25	1.364 (7)
C6—C7	1.401 (6)	C24—H24A	0.9300
C6—H6A	0.9300	C25—C26	1.398 (6)
C7—C8	1.444 (5)	C25—C28	1.490 (7)
C8—C9	1.401 (5)	C26—C27	1.385 (6)
C8—C13	1.403 (5)	C26—H26A	0.9300
C9—C10	1.362 (6)	C28—H28A	0.9600
C9—H9A	0.9300	C28—H28B	0.9600

C10—C11	1.399 (6)	C28—H28C	0.9600
O5···N2	2.806 (4)	C9···C15^{ii}	3.197 (5)
O5···N1	2.852 (4)	C9···C27^{ii}	3.308 (6)
H9A···O1^{ii}	2.60	C6···H9A	2.71
O1···H12A	2.48	C7···H23A^{iv}	2.90
O2···H26A	2.48	C9···H6A	2.72
O3···H12A^{i}	2.58	C20···H23A	2.68
O4···H3A	2.68	C23···H20A	2.67
O4···H1N	2.64	H1N···H3A	2.40
O4···H26A^{i}	2.72	H2N···H17A	2.39
O4···H4A^{iii}	2.60	H6A···H9A	2.17
O5···H1N	1.97	H12A···H14A	2.37
O5···H2N	2.07	H14A···H14A^{v}	2.39
N3···H1N	2.71	H20A···H23A	2.12
C6···C26^{ii}	3.388 (7)	H24A···H28A	2.32
O2^{i}—Cu1—O2	180.0	C12—C13—C8	120.8 (4)
O2^{i}—Cu1—O1	90.74 (11)	C12—C13—C1	119.1 (4)
O2—Cu1—O1	89.26 (11)	C8—C13—C1	120.0 (4)
O2^{i}—Cu1—O1^{i}	89.26 (11)	C11—C14—H14A	109.5
O2—Cu1—O1^{i}	90.74 (11)	C11—C14—H14B	109.5
O1—Cu1—O1^{i}	180.00 (5)	H14A—C14—H14B	109.5
O1—Cu1—O5	90.79 (11)	C11—C14—H14C	109.5
O2—Cu1—O5	94.21 (11)	H14A—C14—H14C	109.5
C1—O1—Cu1	131.4 (2)	H14B—C14—H14C	109.5
C15—O2—Cu1	133.6 (3)	O2—C15—N2	120.7 (4)
C1—N1—C2	124.9 (4)	O2—C15—C27	121.4 (4)
C1—N1—H1N	115.1	N2—C15—C27	117.9 (4)
C2—N1—H1N	119.8	C17—C16—C21	122.8 (4)
C15—N2—C16	124.8 (4)	C17—C16—N2	118.7 (4)
C15—N2—H2N	115.1	C21—C16—N2	118.5 (4)
C16—N2—H2N	119.8	C16—C17—C18	119.2 (5)
O3—N3—O4	123.5 (4)	C16—C17—H17A	120.4
O3—N3—O5	119.9 (4)	C18—C17—H17A	120.4
O4—N3—O5	116.6 (4)	C17—C18—C19	119.3 (6)
O1—C1—N1	121.6 (4)	C17—C18—H18A	120.4
O1—C1—C13	121.1 (4)	C19—C18—H18A	120.4
N1—C1—C13	117.3 (3)	C20—C19—C18	120.3 (5)
C3—C2—C7	121.5 (4)	C20—C19—H19A	119.9
C3—C2—N1	119.2 (4)	C18—C19—H19A	119.9
C7—C2—N1	119.2 (4)	C21—C20—C19	121.9 (5)
C2—C3—C4	119.3 (4)	C21—C20—H20A	119.1
C2—C3—H3A	120.4	C19—C20—H20A	119.1
C4—C3—H3A	120.4	C20—C21—C16	116.6 (5)
C5—C4—C3	120.1 (5)	C20—C21—C22	123.9 (4)
C5—C4—H4A	120.0	C16—C21—C22	119.5 (4)
C3—C4—H4A	120.0	C23—C22—C27	117.6 (4)

C6—C5—C4	120.1 (4)	C23—C22—C21	123.0 (4)
C6—C5—H5A	120.0	C27—C22—C21	119.4 (4)
C4—C5—H5A	120.0	C22—C23—C24	120.2 (5)
C5—C6—C7	121.8 (4)	C22—C23—H23A	119.9
C5—C6—H6A	119.1	C24—C23—H23A	119.9
C7—C6—H6A	119.1	C25—C24—C23	122.0 (4)
C2—C7—C6	117.2 (4)	C25—C24—H24A	119.0
C2—C7—C8	118.7 (4)	C23—C24—H24A	119.0
C6—C7—C8	124.1 (4)	C24—C25—C26	118.4 (5)
C9—C8—C13	116.5 (4)	C24—C25—C28	119.9 (5)
C9—C8—C7	123.7 (4)	C26—C25—C28	121.7 (5)
C13—C8—C7	119.8 (4)	C27—C26—C25	120.7 (4)
C10—C9—C8	121.8 (4)	C27—C26—H26A	119.7
C10—C9—H9A	119.1	C25—C26—H26A	119.7
C8—C9—H9A	119.1	C26—C27—C22	121.0 (4)
C9—C10—C11	121.7 (4)	C26—C27—C15	119.3 (4)
C9—C10—H10A	119.1	C22—C27—C15	119.6 (4)
C11—C10—H10A	119.1	C25—C28—H28A	109.5
C12—C11—C10	117.4 (4)	C25—C28—H28B	109.5
C12—C11—C14	121.7 (4)	H28A—C28—H28B	109.5
C10—C11—C14	120.9 (4)	C25—C28—H28C	109.5
C11—C12—C13	121.7 (4)	H28A—C28—H28C	109.5
C11—C12—H12A	119.1	H28B—C28—H28C	109.5
C13—C12—H12A	119.1		

Cu1—O1—C1—N1	−29.9 (5)	Cu1—O2—C15—N2	−7.3 (6)
Cu1—O1—C1—C13	150.4 (3)	Cu1—O2—C15—C27	171.2 (3)
C2—N1—C1—O1	−178.8 (3)	C16—N2—C15—O2	171.4 (4)
C2—N1—C1—C13	0.9 (5)	C16—N2—C15—C27	−7.1 (6)
C1—N1—C2—C3	179.3 (4)	C15—N2—C16—C17	−175.2 (4)
C1—N1—C2—C7	−1.6 (6)	C15—N2—C16—C21	4.6 (6)
C7—C2—C3—C4	0.6 (6)	C21—C16—C17—C18	−0.7 (8)
N1—C2—C3—C4	179.7 (4)	N2—C16—C17—C18	179.1 (5)
C2—C3—C4—C5	−1.0 (7)	C16—C17—C18—C19	0.7 (8)
C3—C4—C5—C6	1.1 (7)	C17—C18—C19—C20	−0.6 (9)
C4—C5—C6—C7	−0.7 (7)	C18—C19—C20—C21	0.6 (9)
C3—C2—C7—C6	−0.2 (6)	C19—C20—C21—C16	−0.6 (7)
N1—C2—C7—C6	−179.3 (3)	C19—C20—C21—C22	−179.8 (5)
C3—C2—C7—C8	179.3 (4)	C17—C16—C21—C20	0.7 (7)
N1—C2—C7—C8	0.2 (5)	N2—C16—C21—C20	−179.1 (4)
C5—C6—C7—C2	0.3 (6)	C17—C16—C21—C22	179.9 (4)
C5—C6—C7—C8	−179.2 (4)	N2—C16—C21—C22	0.1 (6)
C2—C7—C8—C9	−175.5 (4)	C20—C21—C22—C23	−1.9 (7)
C6—C7—C8—C9	4.0 (6)	C16—C21—C22—C23	178.9 (4)
C2—C7—C8—C13	1.6 (5)	C20—C21—C22—C27	177.5 (4)
C6—C7—C8—C13	−178.9 (4)	C16—C21—C22—C27	−1.7 (6)
C13—C8—C9—C10	3.4 (6)	C27—C22—C23—C24	−2.0 (7)
C7—C8—C9—C10	−179.4 (4)	C21—C22—C23—C24	177.4 (5)

C8—C9—C10—C11	−1.7 (7)	C22—C23—C24—C25	1.0 (8)
C9—C10—C11—C12	−1.0 (6)	C23—C24—C25—C26	1.1 (8)
C9—C10—C11—C14	179.1 (5)	C23—C24—C25—C28	−179.0 (5)
C10—C11—C12—C13	1.9 (6)	C24—C25—C26—C27	−2.0 (7)
C14—C11—C12—C13	−178.3 (4)	C28—C25—C26—C27	178.1 (4)
C11—C12—C13—C8	−0.1 (6)	C25—C26—C27—C22	0.9 (6)
C11—C12—C13—C1	−177.7 (4)	C25—C26—C27—C15	−176.6 (4)
C9—C8—C13—C12	−2.5 (5)	C23—C22—C27—C26	1.1 (6)
C7—C8—C13—C12	−179.8 (4)	C21—C22—C27—C26	−178.4 (4)
C9—C8—C13—C1	175.1 (4)	C23—C22—C27—C15	178.6 (4)
C7—C8—C13—C1	−2.2 (5)	C21—C22—C27—C15	−0.9 (6)
O1—C1—C13—C12	−1.7 (5)	O2—C15—C27—C26	4.1 (6)
N1—C1—C13—C12	178.6 (3)	N2—C15—C27—C26	−177.4 (4)
O1—C1—C13—C8	−179.3 (3)	O2—C15—C27—C22	−173.5 (4)
N1—C1—C13—C8	1.0 (5)	N2—C15—C27—C22	5.1 (6)

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

Hydrogen-bond geometry (Å, º)

*Cg*1, *Cg*3, *Cg*4 and *Cg*5 are the centroids of the (N1/C1/C2/C7/C8/C13), (C2–C7), (C8–C13) and (C16–C21) rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O5	0.90	1.97	2.852 (4)	165
N2—H2*N*···O5	0.90	2.07	2.806 (4)	139
C4—H4*A*···O4^{iii}	0.93	2.60	3.433 (6)	150
C9—H9*A*···O1^{ii}	0.93	2.60	3.514 (5)	169
C12—H12*A*···O3^{i}	0.93	2.57	3.455 (6)	158
C14—H14*C*···*Cg*5^{vi}	0.96	2.92	3.768 (6)	147
C20—H20*A*···*Cg*3^{vii}	0.93	2.86	3.644 (5)	143
C23—H23*A*···*Cg*1^{vii}	0.93	2.89	3.726 (5)	151
C24—H24*A*···*Cg*4^{vii}	0.93	2.77	3.557 (5)	143
C28—H28*C*···*Cg*3^{viii}	0.96	2.88	3.716 (6)	146

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*+1; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) −*x*+1, −*y*, −*z*+1; (vi) *x*, −*y*−1, *z*−1/2; (vii) *x*, *y*+1, *z*; (viii) *x*, −*y*, *z*−1/2.