



Crystal structure and Hirshfeld surface analysis of bis(3-aminopyrazole- κN^1)bis(3-aminopyrazole- κN^2)bis(nitrato- κO)copper(II)

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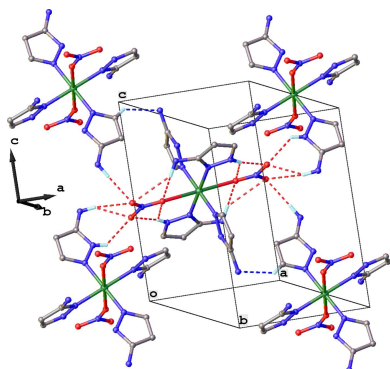
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In the crystal structure of the title compound, [Cu(NO₃)₂(C₃H₅N₃)₄], the Cu^{II} atom is situated on an inversion center (Wyckoff position 2c of space group *P*2₁/*n*) and shows an octahedral [N₄O₂] coordination environment. The axial positions are occupied by O atoms of nitrate anions, while the equatorial positions are taken up by the N atoms of four 3-aminopyrazole ligands. As a result of the tautomerism of the latter, two coordinate with the N¹-atom of 3-aminopyrazole while the other two with the N²-atom. The presence of pyrrole-like N–H groups and amine substituents as donor groups leads to numerous intra- and intermolecular hydrogen-bonding interactions, which were quantified by Hirshfeld surface analysis.

1. Chemical context

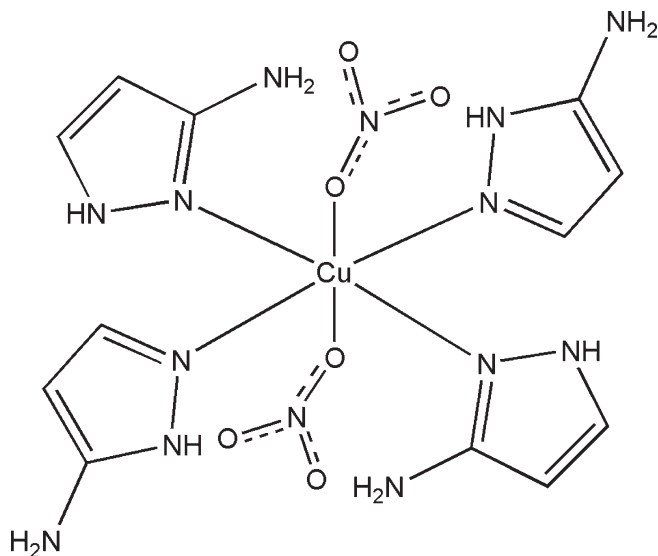
Supramolecular chemistry includes an extensive domain of pyrazole complexes, the main feature of which revolves around the formation of intra- and intermolecular hydrogen bonds (Pérez & Riera, 2009). Pyrazole is a heterocyclic compound that contains two types of N atoms. One of the N atoms is termed pyridine-like because it donates one *p*-electron to the aromatic ring while its lone pair of electrons is non-conjugated. The other N atom is described as acidic pyrrole-like as it contributes two *p*-electrons of the lone pair to the aromatic ring, which consequently is distributed around the ring (Reedijk, 1987).

The presence of both pyridine-like and pyrrole-like N atoms makes a pyrazole molecule both basic and acidic. With respect to the Brønsted–Lowry theory, this ligand is amphoteric. Pyrazolate anions, which are the deprotonated form of pyrazole, form an individual class of ligands which, in contrast to pyrazole itself, can act as bridging. Apart from its ability to donate or accept a proton, an important feature of pyrazole is its tendency to form extensive networks of hydrogen bonds, in particular due to the simultaneous presence of a hydrogen-donating N–H group and a hydrogen-accepting pyridine-like N atom. The existence of these two groups allows the formation of intermolecular N–H...N contacts and makes pyrazole an important molecule for supramolecular chemistry. In addition, numerous examples of practical applications have been offered for pyrazole-containing coordination compounds. For example, copper(II) complexes with pyrazole-containing ligands have been shown to exhibit catalytic (Gamez *et al.*, 2001; Titi *et al.*, 2023), antibacterial (Zaimović *et*



al., 2022), antifungal (Titi *et al.*, 2023) and antitumor (Ruan *et al.*, 2012) activities.

Here we describe the crystal structure of a new copper(II) complex with 3-aminopyrazole as a ligand, namely $[\text{Cu}(\text{C}_3\text{H}_5\text{N}_3)_4(\text{NO}_3)_2]$.



2. Structural commentary

The title compound is a molecular coordination compound, where the central Cu^{II} atom is situated at an inversion center (Wyckoff position 2c of space group $P2_1/n$) with an octahedral $[\text{N}_4\text{O}_2]$ coordination environment. The axial positions are occupied by two oxygen atoms from nitrate ligands [$\text{Cu1}-\text{O2} = 2.5544(19)$ Å, which is a typical value observed in $\text{Cu}-(\text{nitrate})^-$ complexes] and the equatorial positions are occupied by four pyridine-like nitrogen atoms of 3-aminopyrazole (Fig. 1). Two of the four 3-aminopyrazole ligands coordinate with the N^1 atom [$\text{Cu1}-\text{N4} = 1.975(2)$ Å] while the other two coordinate with the N^2 atom [$\text{Cu1}-\text{N1} = 2.0331(17)$ Å]. The different type of N-coordination in the title compound is an illustrative example of tautomerism in 3-aminopyrazole. This effect leads to the formation of more complex and diverse frameworks and expands the potential number of possible coordination compounds that can be formed in comparison with only one type of ligand. The notable difference in the $\text{Cu}-\text{O}$ and $\text{Cu}-\text{N}$ bond lengths leads to an elongation of the coordination octahedron, which is associated with the Jahn–Teller effect that is commonly observed for Cu^{II} complexes. The length distortion parameter $\zeta = |(\text{Cu}-L_i) - \langle \text{Cu}-L \rangle|$ (where $L = \text{ligand}$) for this structure is 1.468 Å. The deviation from an ideal octahedron for twelve *cis*- $L-\text{Cu}-L$ angles can be described by the octahedral distortion parameter $\Sigma = |90^\circ - \alpha_i| = 17.33^\circ$. Pyrazole rings with the same type of coordination are located in one plane, while the angle between pyrazole rings with different types of coordination is $98.67(11)^\circ$. The angle between the CuN_4 and ($\text{N4}/\text{N5}/\text{C4}-\text{C6}$) planes is $16.9(1)^\circ$ while between the CuN_4 and ($\text{N1}/\text{N2}/\text{C1}-\text{C3}$) planes, the corresponding angle is

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H3A}\cdots\text{O3}$	0.96 (4)	2.71 (3)	3.495 (3)	139 (3)
$\text{N3}-\text{H3A}\cdots\text{O2}$	0.96 (4)	1.92 (4)	2.849 (3)	162 (3)
$\text{N3}-\text{H3B}\cdots\text{O3}^{\text{i}}$	0.96 (4)	2.20 (4)	3.085 (3)	153 (3)
$\text{N6}-\text{H6A}\cdots\text{O3}^{\text{ii}}$	0.87 (4)	2.83 (3)	3.480 (3)	132 (3)
$\text{N6}-\text{H6A}\cdots\text{O1}^{\text{ii}}$	0.87 (4)	2.22 (4)	2.999 (3)	149 (3)
$\text{N6}-\text{H6B}\cdots\text{O3}^{\text{iii}}$	0.88 (4)	2.14 (4)	3.019 (3)	176 (3)
$\text{N2}-\text{H2}\cdots\text{N7}^{\text{iv}}$	0.82 (4)	2.60 (4)	3.378 (3)	159 (3)
$\text{N2}-\text{H2}\cdots\text{O1}^{\text{iv}}$	0.82 (4)	2.10 (4)	2.908 (3)	171 (4)
$\text{N2}-\text{H2}\cdots\text{O2}^{\text{iv}}$	0.82 (4)	2.40 (4)	2.999 (3)	131 (3)
$\text{N5}-\text{H5}\cdots\text{O1}^{\text{ii}}$	0.80 (4)	2.47 (4)	3.093 (3)	136 (3)
$\text{N5}-\text{H5}\cdots\text{N3}^{\text{iv}}$	0.80 (4)	2.82 (4)	3.462 (3)	139 (3)
$\text{C6}-\text{H6}\cdots\text{N6}^{\text{v}}$	0.87 (4)	2.70 (4)	3.438 (3)	143 (3)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+1, -y, -z+1$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

$101.48(10)^\circ$. Intramolecular hydrogen bonds stabilize the molecular structure and include $\text{N}-\text{H}\cdots\text{O}$ contacts between 3-aminopyrazole molecules and the O atoms of the nitrate ligand as well as $\text{N}-\text{H}\cdots\text{N}$ contacts between the pyrrole-like N atom of one of the organic ligands and the amino group of another 3-aminopyrazole ligand (Fig. 1, Table 1).

3. Supramolecular features

Molecules of the title coordination compound interact with each other through a set of intermolecular interactions, creating a supramolecular tri-periodic network (Fig. 2). Intermolecular hydrogen bonds include $\text{N}-\text{H}\cdots\text{O}$ contacts between 3-aminopyrazole ligands and nitrate anions of a neighboring complex, as well as weak $\text{C}-\text{H}\cdots\text{N}$ contacts

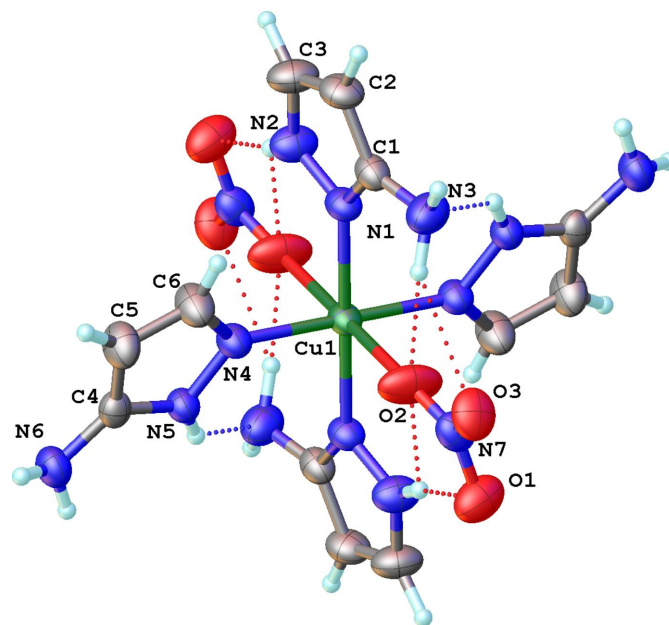


Figure 1

The molecular structure of the title compound showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. Intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are shown as red dotted lines and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds as blue dotted lines. Non-labeled atoms are generated by inversion symmetry [symmetry code: (i) $1-x, -y, 1-z$].

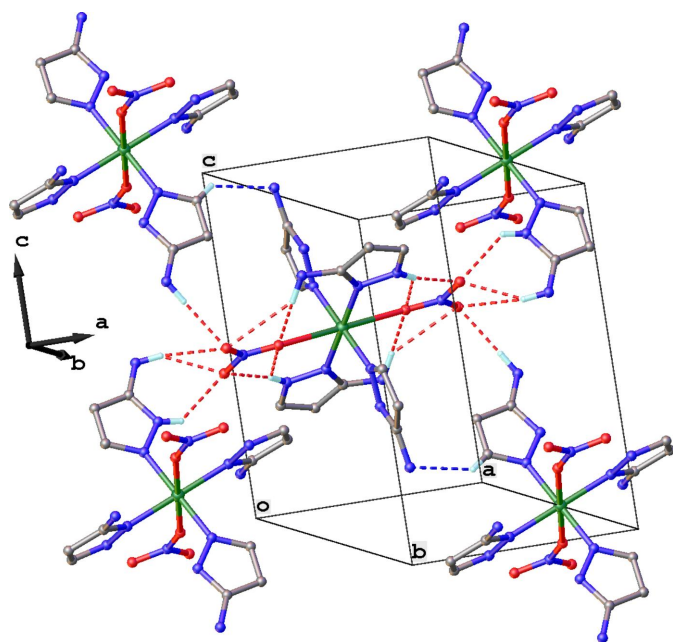


Figure 2
Supramolecular packing of the title compound showing the extended network of weak interactions: N–H···O contacts are shown as red dashed lines and C–H···N contacts as blue dashed lines. N–H···N contacts and H atoms not involved in hydrogen bonding are omitted for clarity.

(Fig. 2). Numerical data of these hydrogen-bonding interactions is collated in Table 1.

4. Hirshfeld surface analysis

A Hirshfeld surface analysis was performed using *Crystal-Explorer* (Spackman *et al.*, 2021) with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed color scale. The associated two-dimensional fingerprint plots were also generated. The Hirshfeld surface of the title compound demonstrates the presence of strong intermolecular N–H···O hydrogen bonds between coordinating nitrate anions and neighboring 3-aminopyrazole molecules, as shown in Fig. 3a in red. Fig. 3b additionally demonstrates the presence of much weaker C–H···N contacts. Fingerprint plots are given for contacts with the highest contribution to the structure (Fig. 3c–f). The most important contributions for the crystal packing are from O···H (32.6%), C···H (14.1%) and N···H (12.9%) contacts. H···H interactions are not shown. The d_e and d_i values presented on the axes of the fingerprint plots are the distances to the closest external and internal atoms from a selected point to the Hirshfeld surface. It is worth noting that the fingerprint plots highlight the most frequently occurring weak interactions within the structure,

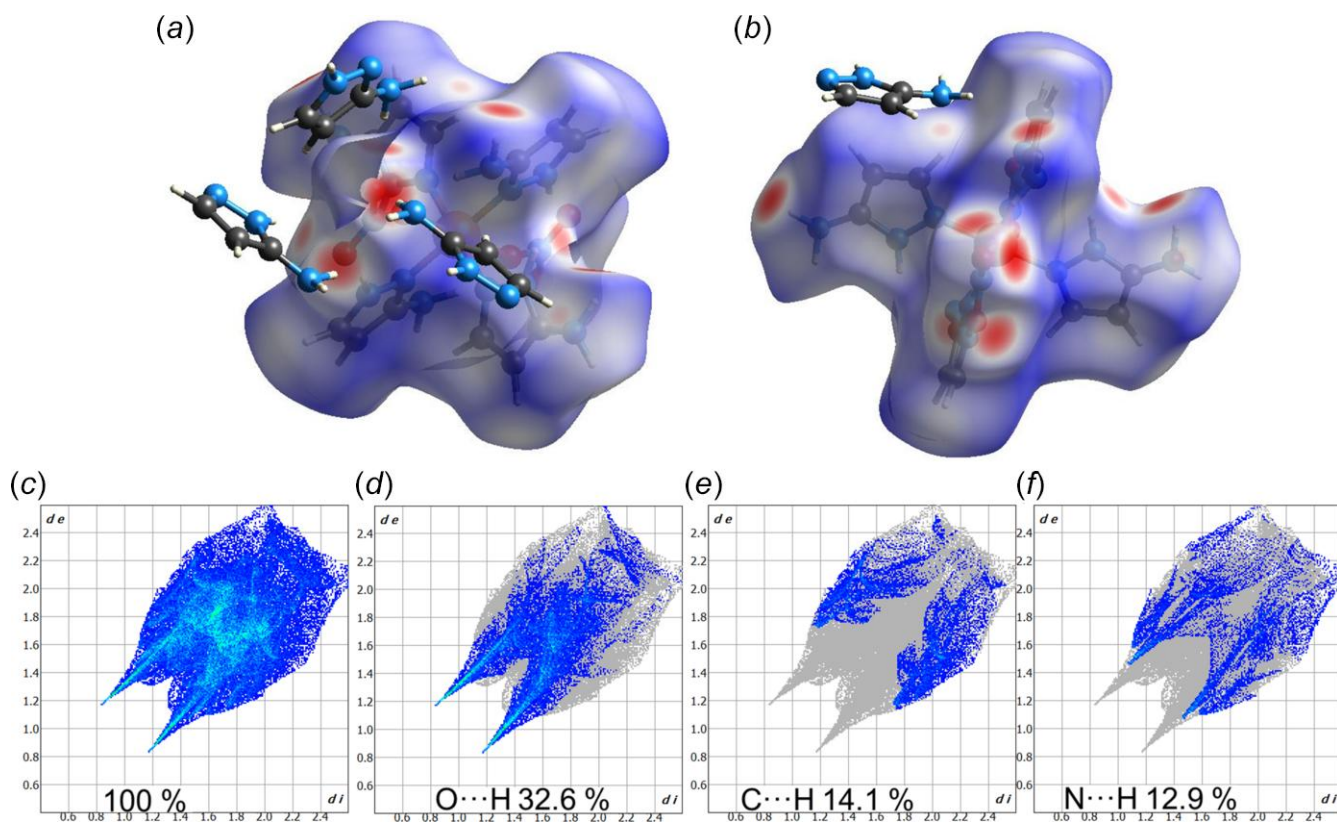


Figure 3
(a), (b) Hirshfeld surface of the title compound plotted over d_{norm} . Neighboring molecules creating contacts with the surface are shown as ‘balls and sticks’; the regions with the strongest intermolecular interactions are plotted in red. (c) Hirshfeld surface fingerprint plots of the title compound showing the contribution of all interactions (100%) and those delineated into (d) O···H, (e) N···H, and (f) C···H interactions.

whereas the graphical depiction of the surface emphasizes the strongest interactions.

5. Database survey

According to a search of the Cambridge Structural Database (CSD, version 5.43, last update March 2022; Groom *et al.*, 2016), there are only two records of copper(II) complexes containing 3-aminopyrazole as a ligand: TIXDAH (Świtlicka-Olszewska *et al.*, 2014) and QIJSAF (Wang *et al.*, 2014). TIXDAH is $[\text{Cu}(\text{C}_2\text{O}_4)(3\text{-aminopyrazole})_2]\cdot 3\text{H}_2\text{O}$, in which Cu^{II} has a square-pyramidal $[\text{N}_3\text{O}_2]$ coordination environment. The basal positions are occupied by the O atoms of a bidentate oxalate anion and two ring N atoms of two aminopyrazole ligands, and the apical positions by the N atom of the amino group of another aminopyrazole ligand. Similar to the title compound, the aminopyrazole molecules display different types of coordination – with N^1 or N^2 atoms. QIJSAF is $[\text{Cu}(3\text{-aminopyrazole})(2,6\text{-pyridinedicarboxylato})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$, in which Cu^{II} has a distorted octahedral $[\text{N}_2\text{O}_4]$ environment. The equatorial positions are occupied by one N^2 -coordinating 3-aminopyrazole and a tridentate 2,6-pyridinedicarboxylate ligand while the axial positions are taken up by one water molecule and one carboxylate O atom of another ligand.

6. Synthesis and crystallization

20 mg (0.1 mmol) of $\text{Cu}(\text{NO}_3)_2$ in 200 μl of water were mixed with 42 mg (0.5 mmol) of 3-aminopyrazole in 200 μl of water. The obtained solution was left to evaporate in air. Within 24 h, blue crystals were collected from the reaction mixture and kept in the mother solution prior to the X-ray measurement.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were found from a difference-Fourier map and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

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Funding information

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Table 2

Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}(\text{NO}_3)_2(\text{C}_3\text{H}_5\text{N}_3)_4]$
M_r	519.96
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	8.83222 (18), 9.9714 (2), 12.1043 (2)
β (°)	97.6408 (19)
V (Å ³)	1056.55 (4)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.05
Crystal size (mm)	0.10 × 0.10 × 0.05
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
$T_{\text{min}}, T_{\text{max}}$	0.631, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6493, 2023, 1903
R_{int}	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.629
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.114, 1.11
No. of reflections	2023
No. of parameters	181
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.45, -0.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

Acta Cryst. (2023). E79, 1100-1103 [https://doi.org/10.1107/S2056989023009295]

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2023); cell refinement: *CrysAlis PRO* (Rigaku OD, 2023); data reduction: *CrysAlis PRO* (Rigaku OD, 2023); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

bis(3-aminopyrazole- κN^1)bis(3-aminopyrazole- κN^2)bis(nitrato- κO)copper(II)

Crystal data

[Cu(NO₃)₂(C₃H₅N₃)₄]
 $M_r = 519.96$
 Monoclinic, $P2_1/n$
 $a = 8.83222$ (18) Å
 $b = 9.9714$ (2) Å
 $c = 12.1043$ (2) Å
 $\beta = 97.6408$ (19)°
 $V = 1056.55$ (4) Å³
 $Z = 2$

$F(000) = 534$
 $D_x = 1.634$ Mg m⁻³
 Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
 Cell parameters from 4669 reflections
 $\theta = 5.0$ – 75.6 °
 $\mu = 2.05$ mm⁻¹
 $T = 200$ K
 Prism, clear light blue
 $0.10 \times 0.10 \times 0.05$ mm

Data collection

XtaLAB Synergy, Dualflex, HyPix
 diffractometer
 Radiation source: micro-focus sealed X-ray
 tube, PhotonJet (Cu) X-ray Source
 Mirror monochromator
 Detector resolution: 10.0000 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.631$, $T_{\max} = 1.000$
 6493 measured reflections
 2023 independent reflections
 1903 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 76.0$ °, $\theta_{\min} = 5.8$ °
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 11$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.114$
 $S = 1.11$
 2023 reflections
 181 parameters
 0 restraints

Hydrogen site location: difference Fourier map
 Only H-atom coordinates refined
 $w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.4789P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.43$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.500000	0.000000	0.500000	0.03217 (18)
N5	0.4258 (2)	−0.05809 (18)	0.72784 (15)	0.0330 (4)
N4	0.3930 (2)	0.01620 (18)	0.63262 (17)	0.0353 (4)
O3	0.7519 (2)	0.40655 (17)	0.58858 (17)	0.0561 (5)
N7	0.7646 (2)	0.28338 (19)	0.59003 (16)	0.0417 (5)
O1	0.8905 (2)	0.2305 (2)	0.6228 (2)	0.0625 (5)
C1	0.3111 (3)	0.2405 (2)	0.38736 (18)	0.0359 (5)
N1	0.3312 (2)	0.11018 (18)	0.41243 (15)	0.0354 (4)
O2	0.6506 (3)	0.2110 (2)	0.5642 (2)	0.0702 (7)
N6	0.3538 (3)	−0.0813 (2)	0.90865 (17)	0.0442 (5)
N2	0.1924 (2)	0.0519 (2)	0.38069 (19)	0.0469 (5)
C4	0.3441 (3)	−0.0178 (2)	0.80771 (19)	0.0341 (5)
C5	0.2547 (3)	0.0873 (3)	0.7639 (2)	0.0488 (6)
C6	0.2881 (3)	0.1034 (3)	0.6570 (2)	0.0498 (6)
C2	0.1602 (3)	0.2639 (3)	0.3389 (2)	0.0443 (5)
C3	0.0907 (3)	0.1423 (3)	0.3363 (2)	0.0516 (6)
N3	0.4272 (3)	0.3290 (2)	0.4016 (2)	0.0530 (5)
H3A	0.499 (4)	0.306 (4)	0.465 (3)	0.064*
H3B	0.400 (4)	0.422 (4)	0.393 (3)	0.064*
H6A	0.434 (4)	−0.132 (4)	0.927 (3)	0.064*
H6B	0.323 (4)	−0.034 (4)	0.962 (3)	0.064*
H2	0.177 (4)	−0.029 (4)	0.385 (3)	0.064*
H5	0.488 (4)	−0.116 (4)	0.731 (3)	0.064*
H3	−0.016 (4)	0.117 (3)	0.296 (3)	0.064*
H6	0.254 (4)	0.165 (4)	0.609 (3)	0.064*
H2A	0.123 (4)	0.346 (4)	0.307 (3)	0.064*
H5A	0.190 (4)	0.135 (4)	0.798 (3)	0.064*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0362 (3)	0.0295 (3)	0.0316 (3)	0.01035 (15)	0.00732 (19)	0.00466 (15)
N5	0.0352 (9)	0.0324 (9)	0.0321 (9)	0.0042 (7)	0.0069 (7)	0.0022 (7)
N4	0.0377 (9)	0.0340 (9)	0.0347 (9)	0.0083 (7)	0.0068 (8)	0.0038 (7)
O3	0.0711 (12)	0.0293 (8)	0.0706 (12)	−0.0027 (8)	0.0197 (10)	0.0045 (8)
N7	0.0518 (12)	0.0323 (10)	0.0403 (10)	−0.0068 (8)	0.0041 (8)	0.0013 (7)
O1	0.0491 (10)	0.0432 (10)	0.0939 (15)	−0.0020 (8)	0.0044 (10)	0.0070 (10)
C1	0.0423 (11)	0.0329 (10)	0.0338 (10)	0.0117 (9)	0.0103 (8)	0.0042 (8)
N1	0.0383 (9)	0.0335 (9)	0.0344 (9)	0.0104 (7)	0.0049 (7)	0.0037 (7)

O2	0.0666 (13)	0.0423 (10)	0.0904 (16)	-0.0113 (9)	-0.0318 (11)	-0.0032 (10)
N6	0.0498 (11)	0.0483 (11)	0.0363 (10)	0.0020 (9)	0.0126 (8)	0.0018 (9)
N2	0.0469 (11)	0.0328 (10)	0.0576 (12)	0.0049 (8)	-0.0053 (9)	0.0004 (9)
C4	0.0344 (11)	0.0327 (10)	0.0362 (11)	-0.0059 (8)	0.0080 (9)	-0.0030 (8)
C5	0.0554 (14)	0.0444 (13)	0.0514 (14)	0.0156 (11)	0.0244 (11)	0.0008 (11)
C6	0.0563 (15)	0.0474 (13)	0.0488 (13)	0.0231 (12)	0.0190 (11)	0.0106 (11)
C2	0.0482 (13)	0.0395 (12)	0.0437 (12)	0.0166 (10)	-0.0001 (10)	0.0048 (10)
C3	0.0455 (14)	0.0462 (14)	0.0579 (15)	0.0099 (11)	-0.0121 (12)	-0.0018 (11)
N3	0.0438 (12)	0.0467 (12)	0.0680 (15)	0.0033 (9)	0.0055 (10)	0.0122 (10)

Geometric parameters (Å, °)

Cu1—N4	1.9748 (19)	N6—C4	1.369 (3)
Cu1—N4 ⁱ	1.9748 (19)	N6—H6A	0.87 (4)
Cu1—N1	2.0331 (17)	N6—H6B	0.88 (4)
Cu1—N1 ⁱ	2.0332 (17)	N2—C3	1.334 (3)
N5—N4	1.368 (3)	N2—H2	0.82 (4)
N5—C4	1.343 (3)	C4—C5	1.375 (3)
N5—H5	0.80 (4)	C5—C6	1.375 (4)
N4—C6	1.332 (3)	C5—H5A	0.88 (3)
O3—N7	1.233 (3)	C6—H6	0.87 (4)
N7—O1	1.247 (3)	C2—C3	1.358 (4)
N7—O2	1.245 (3)	C2—H2A	0.94 (4)
C1—N1	1.340 (3)	C3—H3	1.03 (3)
C1—C2	1.403 (3)	N3—H3A	0.96 (4)
C1—N3	1.347 (3)	N3—H3B	0.96 (4)
N1—N2	1.364 (3)		
N4—Cu1—N4 ⁱ	180.0	H6A—N6—H6B	116 (3)
N4—Cu1—N1 ⁱ	91.01 (7)	N1—N2—H2	123 (3)
N4—Cu1—N1	88.99 (7)	C3—N2—N1	111.0 (2)
N4 ⁱ —Cu1—N1	91.00 (7)	C3—N2—H2	126 (3)
N4 ⁱ —Cu1—N1 ⁱ	89.00 (7)	N5—C4—N6	121.9 (2)
N1—Cu1—N1 ⁱ	180.0	N5—C4—C5	106.7 (2)
N4—N5—H5	120 (2)	N6—C4—C5	131.4 (2)
C4—N5—N4	111.75 (18)	C4—C5—H5A	127 (2)
C4—N5—H5	128 (2)	C6—C5—C4	105.5 (2)
N5—N4—Cu1	124.74 (14)	C6—C5—H5A	127 (2)
C6—N4—Cu1	130.97 (17)	N4—C6—C5	112.0 (2)
C6—N4—N5	104.04 (19)	N4—C6—H6	120 (2)
O3—N7—O1	120.1 (2)	C5—C6—H6	128 (2)
O3—N7—O2	120.3 (2)	C1—C2—H2A	125 (2)
O2—N7—O1	119.5 (2)	C3—C2—C1	105.2 (2)
N1—C1—C2	110.2 (2)	C3—C2—H2A	129 (2)
N1—C1—N3	122.1 (2)	N2—C3—C2	108.4 (2)
N3—C1—C2	127.5 (2)	N2—C3—H3	123 (2)
C1—N1—Cu1	135.03 (16)	C2—C3—H3	127.7 (19)
C1—N1—N2	105.19 (18)	C1—N3—H3A	111 (2)

N2—N1—Cu1	119.06 (14)	C1—N3—H3B	116 (2)
C4—N6—H6A	117 (2)	H3A—N3—H3B	117 (3)
C4—N6—H6B	115 (2)		
Cu1—N4—C6—C5	-173.70 (19)	N6—C4—C5—C6	-176.8 (3)
Cu1—N1—N2—C3	172.49 (18)	C4—N5—N4—Cu1	174.56 (15)
N5—N4—C6—C5	0.5 (3)	C4—N5—N4—C6	-0.1 (3)
N5—C4—C5—C6	0.6 (3)	C4—C5—C6—N4	-0.7 (3)
N4—N5—C4—N6	177.4 (2)	C2—C1—N1—Cu1	-170.29 (17)
N4—N5—C4—C5	-0.3 (3)	C2—C1—N1—N2	-0.6 (2)
C1—N1—N2—C3	0.8 (3)	N3—C1—N1—Cu1	14.0 (3)
C1—C2—C3—N2	0.3 (3)	N3—C1—N1—N2	-176.3 (2)
N1—C1—C2—C3	0.2 (3)	N3—C1—C2—C3	175.6 (3)
N1—N2—C3—C2	-0.7 (3)		

Symmetry code: (i) $-x+1, -y, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3A \cdots O3	0.96 (4)	2.71 (3)	3.495 (3)	139 (3)
N3—H3A \cdots O2	0.96 (4)	1.92 (4)	2.849 (3)	162 (3)
N3—H3B \cdots O3 ⁱⁱ	0.96 (4)	2.20 (4)	3.085 (3)	153 (3)
N6—H6A \cdots O3 ⁱⁱⁱ	0.87 (4)	2.83 (3)	3.480 (3)	132 (3)
N6—H6A \cdots O1 ⁱⁱⁱ	0.87 (4)	2.22 (4)	2.999 (3)	149 (3)
N6—H6B \cdots O3 ^{iv}	0.88 (4)	2.14 (4)	3.019 (3)	176 (3)
N2—H2 \cdots N7 ⁱ	0.82 (4)	2.60 (4)	3.378 (3)	159 (3)
N2—H2 \cdots O1 ⁱ	0.82 (4)	2.10 (4)	2.908 (3)	171 (4)
N2—H2 \cdots O2 ⁱ	0.82 (4)	2.40 (4)	2.999 (3)	131 (3)
N5—H5 \cdots O1 ⁱⁱⁱ	0.80 (4)	2.47 (4)	3.093 (3)	136 (3)
N5—H5 \cdots N3 ⁱ	0.80 (4)	2.82 (4)	3.462 (3)	139 (3)
C6—H6 \cdots N6 ^v	0.87 (4)	2.70 (4)	3.438 (3)	143 (3)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+3/2, y-1/2, -z+3/2$; (iv) $x-1/2, -y+1/2, z+1/2$; (v) $-x+1/2, y+1/2, -z+3/2$.