

Co^{II}-catalysed synthesis of *N*-(4-methoxyphenyl)-5-(pyridin-4-yl)-1,3,4-oxadiazol-2-amine hemihydrochloride monohydrate

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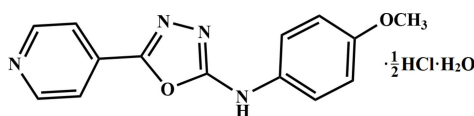
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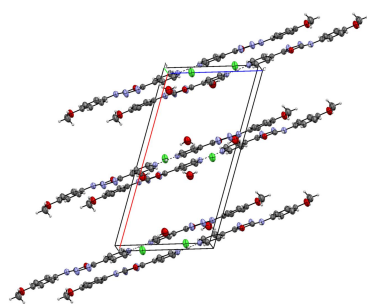
The title compound, C₁₄H₁₂N₄O₂·0.5HCl·H₂O or H(C₁₄H₁₂N₄O₂)₂⁺·Cl⁻·2H₂O, arose from the unexpected cyclization of isonicotinoyl-*N*-phenyl hydrazine carbodithioamide catalysed by cobalt(II) acetate. The organic molecule is almost planar and a symmetric N···H⁺···N hydrogen bond links two of them together, with the H atom lying on a crystallographic twofold axis. The extended structure features N—H···O and O—H···Cl hydrogen bonds, which generate [001] chains. Weak C—H···Cl interactions cross-link the chains. The chloride ion has site symmetry 2. The major contributions to the Hirshfeld surface are from H···H (47.1%), Cl···H/H···Cl (total 10.8%), O···H/H···O (7.4%) and N···H/H···N (6.7%) interactions.

1. Chemical context

1,3,4-Oxadiazole derivatives have been studied in recent years for their diverse biological activities (Gond *et al.*, 2023; Abd-Ellah *et al.*, 2017; Bitla *et al.*, 2020). As a result of their electron-accepting properties, high quantum yield, and good thermal and chemical stabilities, they have also been used in electroluminescent, optical and electron-transporting materials and chelating agents (Najare *et al.*, 2020; Wu *et al.*, 2012). Several methods for the synthesis of 1,3,4-oxadiazoles from acyclic precursors are available, which include oxidative cyclization of acylhydrazones (Jedlovská & Leško, 1994) and acylthiosemicarbazides (Omar *et al.*, 1996, Paswan *et al.*, 2015). In the presence of a strong acid, an *N*-acylhydrazine carbodithioate is converted into a thiadiazole whereas in the presence of a weak acid or base or on complexation they can be cyclized into oxadiazole (Reid & Heindel, 1976; Jasinski *et al.*, 2011).



We have previously reported the cyclo-desulfurization of several *N*-acylhydrazine carbodithioates into the corresponding 1,3,4-oxadiazole in the presence of manganese(II) acetate *via* the loss of H₂S where the Mn^{II} ion presumably behaves as a weak Lewis acid (Paswan *et al.*, 2015, 2016; Gond *et al.*, 2022). In the present work, a similar reaction is reported in presence of Co^{II} chloride. Similar Co^{II}-assisted cyclization reactions are also reported in the literature (Li *et al.*, 2021, 2023; Bharty *et al.*, 2012).



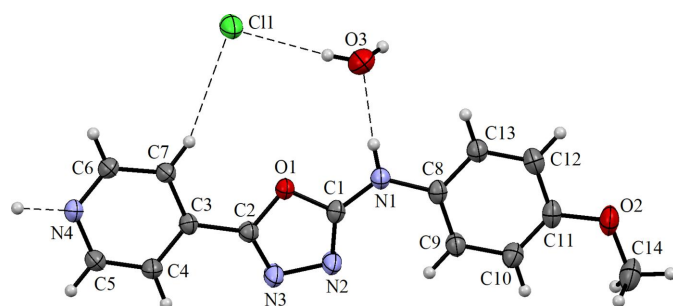


Figure 1
The molecular structure of the title compound showing 30% probability displacement ellipsoids with hydrogen bonds indicated by dashed lines.

2. Structural commentary

The compound crystallizes in the monoclinic crystal system in space group $C2/c$. The asymmetric unit consists of one organic molecule, half an equivalent of HCl and one water molecule (Fig. 1). The C3–C7/N4 pyridyl, C1/C2/N2/N3/O1 oxadiazole and C8–C13 phenyl rings are close to co-planar with the dihedral angles between pyridyl and oxadiazole rings being $4.88(9)^\circ$, oxadiazole and phenyl rings $4.27(10)^\circ$ and pyridyl and phenyl rings $2.27(9)^\circ$. The bond distances and angles of the 1,3,4-oxadiazole ring [C1–N2 = $1.298(2)$; C2–N3 = $1.277(2)$ Å] are in good agreement with values reported previously (Jasinski *et al.*, 2011; Paswan *et al.*, 2015, 2016; Singh

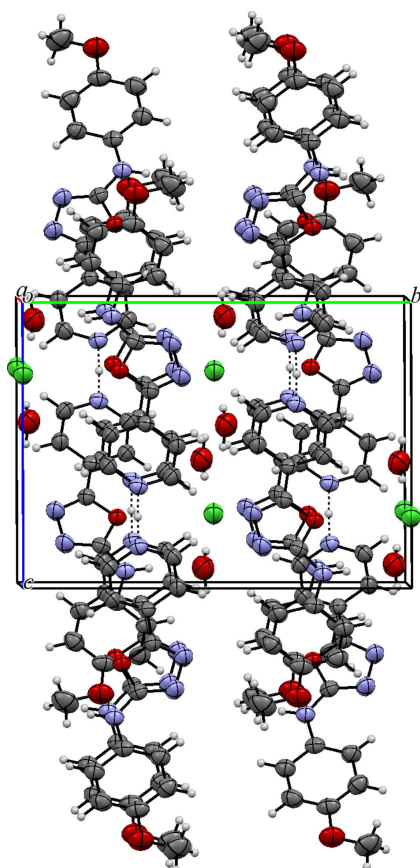


Figure 2
The packing of the title compound viewed along the a -axis direction.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4–H4N \cdots N4 ⁱ	1.34 (1)	1.34 (1)	2.675 (3)	178 (3)
N1–H1 \cdots O3	0.86	2.02	2.875 (2)	172
O3–H22 \cdots Cl1	0.82 (4)	2.43 (4)	3.233 (2)	166 (3)
O3–H21 \cdots Cl1 ⁱⁱ	0.81 (4)	2.55 (4)	3.359 (3)	172 (4)
C7–H7 \cdots Cl1	0.93	2.93	3.7940 (18)	155
C6–H6 \cdots Cl1 ⁱⁱⁱ	0.93	2.82	3.7137 (18)	163
C5–H5 \cdots N3 ^{iv}	0.93	2.56	3.329 (2)	140
C9–H9 \cdots N2	0.93	2.34	2.969 (2)	125

Symmetry codes: (i) $-x+1, y, -z+\frac{5}{2}$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $x, -y, z+\frac{1}{2}$.

et al., 2007). The C–N bond distance in the pyridine ring, C5–N4 = $1.336(2)$ Å, is slightly longer than the corresponding bond in a similar compound ($1.326(2)$ Å; Singh *et al.*, 2006), probably due to the N \cdots H interaction (Fig. 2).

3. Supramolecular features

In the extended structure, two organic molecules are linked through their pyridine nitrogen atoms *via* the proton of the hydrochloric acid, which lies on a crystallographic twofold axis. This strong, symmetrical, almost linear N4 \cdots H4N \cdots N4 hydrogen bond (Table 1) leads to a rod-like dimeric structure. These units form a layer-like structure when viewed along b axis of the unit cell (Fig. 3). The water molecules and chloride ions (site symmetry 2) are embedded in the space between the chains and are connected to them *via* N–H \cdots O and O–H \cdots Cl hydrogen bonds, thereby generating [001] chains. Weak C–H \cdots Cl interactions are also observed (Table 1; Fig. 2).

4. Hirshfeld Surface Analysis

To gain further insight into the intermolecular interactions, a Hirshfeld surface analysis was performed using *Crystal*

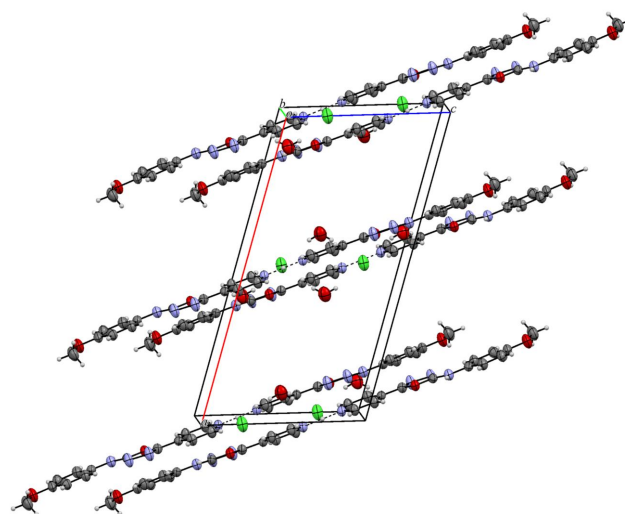
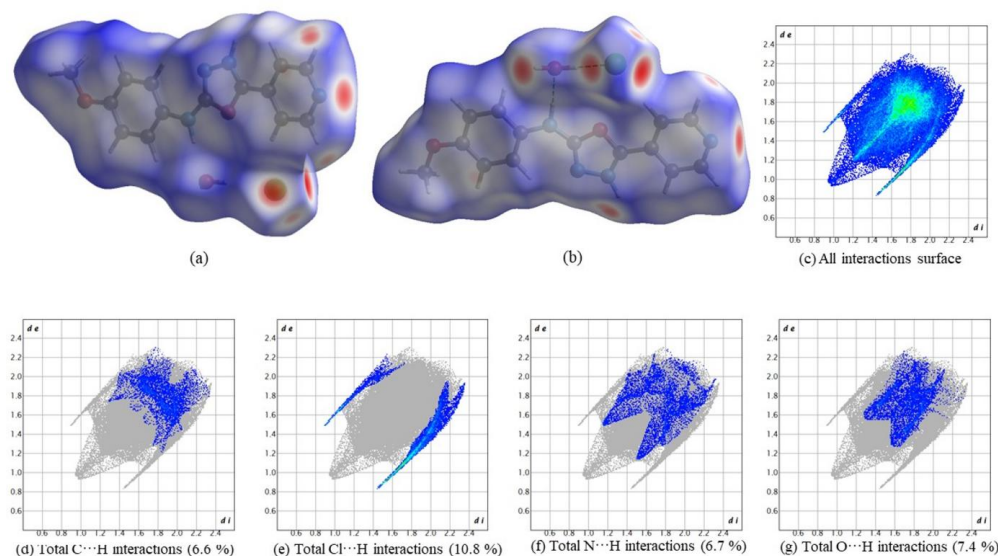


Figure 3
The packing of title compound viewed along the b -axis direction.


Figure 4

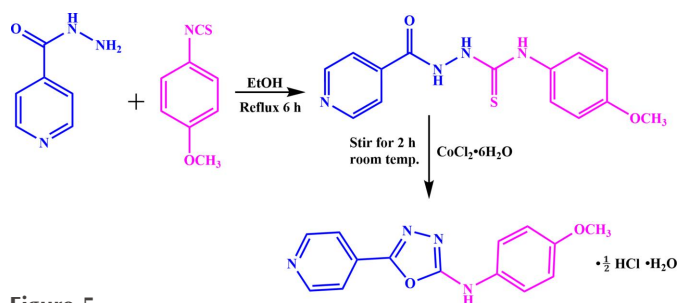
(a), (b) Two views of the Hirshfeld surface of the title compound mapped over d_{norm} , (c) fingerprint plot showing the total contribution of individual interactions and those delineated into (d) C...H/H...C interactions (6.6%), (e) Cl...H/H...Cl interactions (10.8%), (f) N...H/H...N interactions (6.7%) and (g) O...H/H...O interactions (7.4%).

Explorer 17.5 (Spackman *et al.*, 2021). Fig. 4a,b shows the Hirshfeld surface mapped over d_{norm} . The red spots show the various hydrogen bonds noted above.

The two-dimensional fingerprint plots are presented in Fig. 4c–g. The H...H (van der Waals) contacts dominate at 47.1%. Among the directional interactions present in the structure, the Cl...H/H...Cl (total 10.8%) contact is the most significant. Other contacts include 6.6% for C...H/H...C, 6.7% N...H/H...N and 7.4% for O...H/H...O interactions.

5. Synthesis and crystallization

2-Isonicotinoyl-*N*-(4-methoxyphenyl)hydrazine-1-carbothioamide was prepared by adding 1.652 g (10.00 mmol) of 4-methoxy phenyl isothiocyanate in ethanol solution to 1.370 g (10.00 mmol) of isonicotinohydrazide and the reaction mixture was refluxed for 6 h at 333 K. Upon cooling, a white precipitate of 2-isonicotinoyl-*N*-(4-methoxyphenyl)hydrazine-1-carbothioamide was obtained (Fig. 5), which was filtered off and washed with a 50:50 *v/v* mixture of water and ether. Then, 1.00 mmol of 2-isonicotinoyl-*N*-(4-methoxyphenyl)hydrazine-


Figure 5

Synthesis scheme for the title compound.

1-carbothioamide was dissolved in a 50:50 *v/v* mixture of methanol and chloroform, and a methanolic solution of 0.5 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added and stirred for 2 h, during which time the smell of H_2S was noted. The clear solution obtained was kept for crystallization and after 15 days, pale-pink blocks of the title compound were grown. Yield: 60.6%; m.p. 495–498 K. Analysis calculated for $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2 \cdot 0.5 \text{HCl} \cdot \text{H}_2\text{O}$: C, 55.21; H, 4.79; N, 18.39%; found: C, 55.25; H, 4.50; N, 18.55%.

The IR spectrum (KBr disc) shows an absorption band at 3280 cm^{-1} due to the NH group. The C=O band is absent and a new band is observed at 1623 cm^{-1} corresponding to the C=N bond. In addition, a blue shift is observed for the N=N band at 1179 cm^{-1} compared to the single bond in the thiosemicarbazide intermediate (Fig. 1 in the supporting information). All these data indicate that the carbothioamide moiety has been transformed into the corresponding oxadiazole (Chandra *et al.*, 2022; Jaiswal *et al.*, 2023ab).

The ^1H NMR spectrum of the title compound in $\text{DMSO}-d_6$ displays peaks at δ 10.69 ppm due to the NH proton, at δ 8.91 and 7.90 ppm due to the pyridyl ring protons and at δ 7.55 and 6.98 ppm due to phenyl ring protons. The methoxy protons appear at δ 3.74 ppm. (Fig. 2 in the supporting information). In the ^{13}C NMR spectrum, peaks at δ 156.9 and 155.2 ppm arise from oxadiazole ring carbon atoms, the methoxy C atom appears at 55.7 ppm and the phenyl and pyridyl carbon atoms are observed in the range δ 114.8–132.4 ppm (Fig. 3 in the supporting information). An absorption at 338 nm in the electronic spectrum of the title compound can be attributed to its π - π^* transition (Fig. 4 in the supporting information). It displays fluorescence at 418 nm upon excitation at 338 nm (Fig. 5 in the supporting information) when dissolved in 10^{-5} M DMSO solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atom H4N was freely refined. Other H atoms were placed in idealized locations (N—H = 0.86 Å, C—H = 0.93–0.96 Å) and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{C-methyl})$. Asymmetric N—H...N/N...H—N refinements with the H atom displaced towards one of the N atoms were inconclusive and atom H4N was placed on the twofold axis.

Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{28}\text{H}_{25}\text{N}_8\text{O}_4 \cdot \text{Cl}^- \cdot 2\text{H}_2\text{O}$
M_r	609.04
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	293
a, b, c (Å)	20.5406 (9), 13.7457 (5), 10.5650 (3)
β (°)	107.006 (4)
V (Å ³)	2852.54 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.19
Crystal size (mm)	0.32 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker multiwire proportional
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16772, 3121, 2026
R_{int}	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.119, 0.98
No. of reflections	3009
No. of parameters	205
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.20, -0.18

Computer programs: FRAMBO (Bruker, 2004), SHELXTL (Sheldrick, 2008) and SHELXL2018/3 (Sheldrick, 2015).

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supporting information

Acta Cryst. (2024). E80, 351-354 [https://doi.org/10.1107/S2056989024002044]

Co^{II}-catalysed synthesis of *N*-(4-methoxyphenyl)-5-(pyridin-4-yl)-1,3,4-oxadiazol-2-amine hemihydrochloride monohydrate

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Computing details

N-(4-Methoxyphenyl)-5-(pyridin-4-yl)-1,3,4-oxadiazol-2-amine 4-{5-[(4-methoxyphenyl)amino]-1,3,4-oxadiazol-2-yl}pyridin-1-ium chloride dihydrate

Crystal data

C₂₈H₂₅N₈O₄⁺·Cl⁻·2H₂O

M_r = 609.04

Monoclinic, *C*2/*c*

a = 20.5406 (9) Å

b = 13.7457 (5) Å

c = 10.5650 (3) Å

β = 107.006 (4)°

V = 2852.54 (19) Å³

Z = 4

F(000) = 1276

D_x = 1.418 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 8519 reflections

θ = 2.5–26.2°

μ = 0.19 mm⁻¹

T = 293 K

Block, pinkish

0.32 × 0.26 × 0.24 mm

Data collection

Bruker multiwire proportional diffractometer

Radiation source: sealed tube phi and ω scans

16772 measured reflections

3121 independent reflections

2026 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.029

θ_{max} = 27.0°, θ_{min} = 2.5°

h = -25→25

k = -17→13

l = -13→11

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.041

wR(*F*²) = 0.119

S = 0.98

3009 reflections

205 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F*_o²) + (0.0602*P*)² + 1.1461*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.20 e Å⁻³

Δρ_{min} = -0.18 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.500000	0.49848 (5)	0.750000	0.0696 (3)
O1	0.60240 (6)	0.24882 (8)	0.73971 (10)	0.0438 (3)
O2	0.73500 (8)	0.20297 (12)	0.12535 (14)	0.0738 (4)
N4	0.52376 (7)	0.20300 (10)	1.14485 (13)	0.0447 (4)
N1	0.63480 (7)	0.26868 (11)	0.55203 (13)	0.0470 (4)
H1	0.627028	0.329212	0.562248	0.056*
N2	0.62683 (8)	0.11322 (11)	0.64893 (14)	0.0567 (4)
O3	0.59808 (11)	0.46965 (13)	0.5629 (3)	0.0817 (5)
N3	0.60728 (9)	0.08972 (11)	0.76220 (15)	0.0579 (4)
C3	0.57017 (8)	0.18290 (12)	0.92666 (15)	0.0395 (4)
C1	0.62287 (8)	0.20733 (13)	0.64050 (15)	0.0423 (4)
C2	0.59381 (8)	0.16960 (12)	0.81088 (16)	0.0421 (4)
C7	0.55180 (9)	0.27308 (13)	0.96298 (16)	0.0465 (4)
H7	0.554704	0.328207	0.913884	0.056*
C8	0.65878 (8)	0.24517 (13)	0.44342 (16)	0.0438 (4)
C6	0.52914 (9)	0.27987 (13)	1.07303 (16)	0.0481 (4)
H6	0.517179	0.340647	1.097866	0.058*
C4	0.56536 (9)	0.10281 (13)	1.00308 (17)	0.0489 (4)
H4	0.577659	0.041269	0.981505	0.059*
C5	0.54218 (9)	0.11591 (13)	1.11088 (17)	0.0504 (5)
H5	0.539154	0.062199	1.162390	0.060*
C13	0.66769 (10)	0.32122 (14)	0.36423 (17)	0.0526 (5)
H13	0.656561	0.384241	0.382362	0.063*
C11	0.70949 (9)	0.21120 (15)	0.23119 (17)	0.0537 (5)
C9	0.67449 (9)	0.15188 (14)	0.41413 (17)	0.0514 (5)
H9	0.668165	0.100040	0.465852	0.062*
C12	0.69280 (10)	0.30451 (15)	0.25909 (19)	0.0578 (5)
H12	0.698590	0.356168	0.206558	0.069*
C10	0.69972 (10)	0.13515 (15)	0.30768 (18)	0.0560 (5)
H10	0.710046	0.072074	0.288146	0.067*
C14	0.75778 (13)	0.11035 (19)	0.0984 (2)	0.0827 (7)
H14A	0.774283	0.114498	0.022456	0.124*
H14B	0.793818	0.088726	0.173472	0.124*
H14C	0.720706	0.064931	0.081080	0.124*
H22	0.5797 (18)	0.477 (2)	0.621 (3)	0.129 (14)*
H21	0.578 (2)	0.478 (3)	0.485 (4)	0.159 (18)*
H4N	0.500000	0.205 (2)	1.250000	0.092 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1079 (7)	0.0494 (4)	0.0619 (4)	0.000	0.0413 (4)	0.000
O1	0.0531 (7)	0.0434 (7)	0.0391 (6)	0.0010 (5)	0.0201 (5)	-0.0004 (5)
O2	0.0879 (11)	0.0901 (11)	0.0591 (8)	0.0004 (9)	0.0458 (8)	-0.0021 (8)
N4	0.0507 (9)	0.0484 (9)	0.0375 (7)	0.0013 (7)	0.0168 (6)	-0.0010 (6)

N1	0.0547 (9)	0.0476 (8)	0.0434 (8)	-0.0006 (7)	0.0218 (7)	0.0003 (7)
N2	0.0838 (12)	0.0460 (10)	0.0518 (9)	-0.0039 (8)	0.0380 (8)	-0.0053 (7)
O3	0.1057 (15)	0.0670 (11)	0.0814 (13)	0.0140 (9)	0.0413 (13)	-0.0026 (9)
N3	0.0875 (12)	0.0457 (9)	0.0520 (9)	-0.0028 (8)	0.0386 (9)	-0.0040 (7)
C3	0.0413 (9)	0.0428 (9)	0.0346 (8)	-0.0022 (7)	0.0115 (7)	-0.0011 (7)
C1	0.0421 (9)	0.0488 (10)	0.0371 (9)	-0.0036 (8)	0.0133 (7)	-0.0054 (7)
C2	0.0471 (10)	0.0406 (9)	0.0395 (9)	-0.0022 (7)	0.0141 (8)	-0.0009 (7)
C7	0.0604 (11)	0.0395 (9)	0.0421 (9)	0.0029 (8)	0.0189 (8)	0.0033 (7)
C8	0.0408 (9)	0.0546 (11)	0.0361 (8)	-0.0040 (8)	0.0116 (7)	-0.0016 (8)
C6	0.0597 (11)	0.0424 (10)	0.0457 (10)	0.0045 (8)	0.0209 (9)	-0.0018 (8)
C4	0.0628 (12)	0.0398 (10)	0.0493 (10)	0.0033 (8)	0.0245 (9)	0.0018 (8)
C5	0.0633 (12)	0.0445 (10)	0.0476 (10)	0.0016 (9)	0.0228 (9)	0.0079 (8)
C13	0.0592 (12)	0.0552 (11)	0.0469 (10)	-0.0007 (9)	0.0208 (9)	0.0019 (8)
C11	0.0504 (11)	0.0751 (14)	0.0397 (9)	-0.0067 (9)	0.0195 (8)	-0.0036 (9)
C9	0.0597 (12)	0.0548 (12)	0.0446 (10)	-0.0049 (9)	0.0231 (9)	0.0002 (8)
C12	0.0639 (13)	0.0655 (13)	0.0484 (10)	-0.0049 (10)	0.0235 (9)	0.0070 (9)
C10	0.0595 (12)	0.0595 (12)	0.0534 (11)	-0.0021 (9)	0.0236 (9)	-0.0085 (9)
C14	0.0935 (18)	0.0996 (19)	0.0706 (14)	-0.0045 (15)	0.0485 (13)	-0.0172 (13)

Geometric parameters (Å, °)

O1—C1	1.3634 (19)	C7—H7	0.9300
O1—C2	1.3637 (19)	C8—C9	1.379 (3)
O2—C11	1.371 (2)	C8—C13	1.384 (2)
O2—C14	1.414 (3)	C6—H6	0.9300
N4—C6	1.324 (2)	C4—C5	1.369 (2)
N4—C5	1.336 (2)	C4—H4	0.9300
N4—H4N	1.3379 (15)	C5—H5	0.9300
N1—C1	1.334 (2)	C13—C12	1.374 (3)
N1—C8	1.412 (2)	C13—H13	0.9300
N1—H1	0.8600	C11—C10	1.371 (3)
N2—C1	1.298 (2)	C11—C12	1.382 (3)
N2—N3	1.407 (2)	C9—C10	1.388 (2)
O3—H22	0.82 (4)	C9—H9	0.9300
O3—H21	0.81 (4)	C12—H12	0.9300
N3—C2	1.277 (2)	C10—H10	0.9300
C3—C7	1.382 (2)	C14—H14A	0.9600
C3—C4	1.386 (2)	C14—H14B	0.9600
C3—C2	1.454 (2)	C14—H14C	0.9600
C7—C6	1.376 (2)		
C1—O1—C2	102.04 (13)	C7—C6—H6	118.8
C11—O2—C14	117.79 (17)	C5—C4—C3	118.79 (16)
C6—N4—C5	118.91 (15)	C5—C4—H4	120.6
C6—N4—H4N	124.9 (13)	C3—C4—H4	120.6
C5—N4—H4N	116.2 (13)	N4—C5—C4	122.43 (16)
C1—N1—C8	127.16 (15)	N4—C5—H5	118.8
C1—N1—H1	116.4	C4—C5—H5	118.8

C8—N1—H1	116.4	C12—C13—C8	120.64 (18)
C1—N2—N3	105.04 (14)	C12—C13—H13	119.7
H22—O3—H21	122 (4)	C8—C13—H13	119.7
C2—N3—N2	107.14 (14)	C10—C11—O2	125.05 (19)
C7—C3—C4	118.62 (16)	C10—C11—C12	119.59 (17)
C7—C3—C2	122.13 (15)	O2—C11—C12	115.36 (18)
C4—C3—C2	119.25 (15)	C8—C9—C10	120.20 (18)
N2—C1—N1	131.13 (16)	C8—C9—H9	119.9
N2—C1—O1	113.05 (14)	C10—C9—H9	119.9
N1—C1—O1	115.82 (15)	C13—C12—C11	120.19 (18)
N3—C2—O1	112.73 (15)	C13—C12—H12	119.9
N3—C2—C3	127.75 (15)	C11—C12—H12	119.9
O1—C2—C3	119.50 (14)	C11—C10—C9	120.31 (19)
C6—C7—C3	118.86 (16)	C11—C10—H10	119.8
C6—C7—H7	120.6	C9—C10—H10	119.8
C3—C7—H7	120.6	O2—C14—H14A	109.5
C9—C8—C13	119.05 (17)	O2—C14—H14B	109.5
C9—C8—N1	123.71 (16)	H14A—C14—H14B	109.5
C13—C8—N1	117.23 (16)	O2—C14—H14C	109.5
N4—C6—C7	122.38 (16)	H14A—C14—H14C	109.5
N4—C6—H6	118.8	H14B—C14—H14C	109.5
C1—N2—N3—C2	-0.2 (2)	C5—N4—C6—C7	1.3 (3)
N3—N2—C1—N1	-179.21 (18)	C3—C7—C6—N4	-0.6 (3)
N3—N2—C1—O1	0.22 (19)	C7—C3—C4—C5	0.5 (3)
C8—N1—C1—N2	-3.2 (3)	C2—C3—C4—C5	-179.14 (16)
C8—N1—C1—O1	177.42 (14)	C6—N4—C5—C4	-1.2 (3)
C2—O1—C1—N2	-0.20 (18)	C3—C4—C5—N4	0.3 (3)
C2—O1—C1—N1	179.33 (14)	C9—C8—C13—C12	-1.0 (3)
N2—N3—C2—O1	0.0 (2)	N1—C8—C13—C12	178.02 (16)
N2—N3—C2—C3	178.69 (16)	C14—O2—C11—C10	-5.0 (3)
C1—O1—C2—N3	0.08 (18)	C14—O2—C11—C12	175.28 (18)
C1—O1—C2—C3	-178.69 (14)	C13—C8—C9—C10	0.9 (3)
C7—C3—C2—N3	-174.38 (18)	N1—C8—C9—C10	-178.10 (15)
C4—C3—C2—N3	5.2 (3)	C8—C13—C12—C11	0.0 (3)
C7—C3—C2—O1	4.2 (2)	C10—C11—C12—C13	1.1 (3)
C4—C3—C2—O1	-176.23 (15)	O2—C11—C12—C13	-179.10 (17)
C4—C3—C7—C6	-0.3 (3)	O2—C11—C10—C9	178.98 (18)
C2—C3—C7—C6	179.26 (15)	C12—C11—C10—C9	-1.3 (3)
C1—N1—C8—C9	-0.8 (3)	C8—C9—C10—C11	0.3 (3)
C1—N1—C8—C13	-179.82 (16)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N4—H4N \cdots N4 ⁱ	1.34 (1)	1.34 (1)	2.675 (3)	178 (3)
N1—H1 \cdots O3	0.86	2.02	2.875 (2)	172
O3—H22 \cdots C11	0.82 (4)	2.43 (4)	3.233 (2)	166 (3)

O3—H21…C11 ⁱⁱ	0.81 (4)	2.55 (4)	3.359 (3)	172 (4)
C7—H7…C11	0.93	2.93	3.7940 (18)	155
C6—H6…C11 ⁱⁱⁱ	0.93	2.82	3.7137 (18)	163
C5—H5…N3 ^{iv}	0.93	2.56	3.329 (2)	140
C9—H9…N2	0.93	2.34	2.969 (2)	125

Symmetry codes: (i) $-x+1, y, -z+5/2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $x, -y, z+1/2$.