

2-Amino-3-nitropyridinium perrhenate

Zeid Abdellah Al Othman,^a Samah Toumi Akriche,^{b*}
Mohamed Rzaigui^b and Refaat Mohamed Mahfouz^a

^aChemistry Department, Faculty of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia, and ^bLaboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna Bizerte, Tunisia

Correspondence e-mail: toumiakriche@yahoo.fr

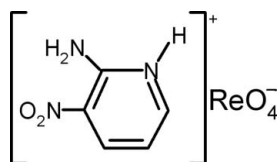
Received 13 May 2010; accepted 16 May 2010

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.015$ Å; R factor = 0.040; wR factor = 0.111; data-to-parameter ratio = 34.2.

In the title molecular salt, $(\text{C}_5\text{H}_6\text{N}_3\text{O}_2)[\text{ReO}_4]$, the cations and tetrahedral anions are linked by trifurcated $\text{N}-\text{H}\cdots(\text{O},\text{O},\text{O})$ and bifurcated $\text{N}-\text{H}\cdots(\text{O},\text{O})$ hydrogen bonds, as well as weak $\text{C}-\text{H}\cdots\text{O}$ interactions. This results in alternating corrugated inorganic and organic layers in the crystal.

Related literature

For hydrogen-bond interactions see: Katayev *et al.* (2006). For related structures containing 2-amino-3-nitropyridinium cations, see: Akriche & Rzaigui (2000, 2009); Toumi Akriche *et al.* (2010). For related structures containing perrhenate anions, see: Rodrigues *et al.* (2009); Ray *et al.* (2002, 2003). For distortion indices, see: Baur (1974).



Experimental

Crystal data

$(\text{C}_5\text{H}_6\text{N}_3\text{O}_2)[\text{ReO}_4]$

$M_r = 390.33$

Monoclinic, $P2_1/c$

$a = 6.235$ (3) Å

$b = 22.030$ (2) Å

$c = 7.840$ (6) Å

$\beta = 117.52$ (5)°

$V = 955.0$ (9) Å³

$Z = 4$

Ag $K\alpha$ radiation

$\lambda = 0.56087$ Å

$\mu = 6.86$ mm⁻¹

$T = 293$ K

$0.50 \times 0.40 \times 0.30$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Absorption correction: multi-scan
(Blessing, 1995)

$T_{\min} = 0.054$, $T_{\max} = 0.134$

7565 measured reflections

4682 independent reflections

3532 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

2 standard reflections every 120 min

intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.111$

$S = 1.07$

4682 reflections

137 parameters

24 restraints

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 2.71$ e Å⁻³

$\Delta\rho_{\text{min}} = -2.35$ e Å⁻³

Table 1

Selected bond lengths (Å).

Re1—O1	1.726 (6)	Re1—O3	1.708 (8)
Re1—O2	1.706 (7)	Re1—O4	1.665 (7)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 ⁱ ⋯O1	0.86	2.37	3.041 (10)	135
N1—H1 ⁱ ⋯O2 ⁱ	0.86	2.42	3.018 (10)	128
N1—H1 ⁱ ⋯O1 ⁱⁱ	0.86	2.48	3.077 (11)	128
N2—H2A ⁱ ⋯O1	0.86	2.38	3.036 (10)	133
N2—H2A ⁱ ⋯O1 ⁱⁱ	0.86	2.40	3.010 (10)	129
N2—H2A ⁱ ⋯O2 ⁱⁱⁱ	0.86	2.55	3.168 (11)	129
N2—H2B ⁱ ⋯O5	0.86	2.02	2.624 (11)	127
N2—H2B ⁱ ⋯O3 ⁱⁱⁱ	0.86	2.26	2.976 (12)	141
C3—H3 ⁱ ⋯O5 ^{iv}	0.93	2.44	3.138 (12)	132
C5—H5 ⁱ ⋯O4 ^v	0.93	2.32	3.094 (13)	141
C5—H5 ⁱ ⋯O2 ⁱ	0.93	2.41	3.020 (13)	123

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5451).

References

- Akriche, S. & Rzaigui, M. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 617–618.
- Akriche, S. & Rzaigui, M. (2009). *Acta Cryst.* **E65**, o1648.
- Baur, W. H. (1974). *Acta Cryst.* **B30**, 1195–1215.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Katayev, E. A., Ustynuk, Y. A. & Sessler, J. L. (2006). *Coord. Chem. Rev.* **250**, 3004–3037.
- Ray, U., Chand, B., Dasmahapatra, A. K., Mostafa, G., Lu, T. H. & Sinha, C. (2003). *Inorg. Chem. Commun.* **6**, 634–638.
- Ray, U. S., Mostafa, G., Lu, T. H. & Sinha, C. (2002). *Cryst. Eng.* **5**, 95–104.
- Rodrigues, V. H., Costa, M. M. R. R., Dekola, T. & de Matos Gomes, E. (2009). *Acta Cryst.* **E65**, m19.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Toumi Akriche, S., Rzaigui, M., Al-Hokbany, N. & Mahfouz, R. M. (2010). *Acta Cryst.* **E66**, o300.

supporting information

Acta Cryst. (2010). E66, m689 [https://doi.org/10.1107/S160053681001812X]

2-Amino-3-nitropyridinium perrhenate

Zeid Abdellah Al Othman, Samah Toumi Akriche, Mohamed Rzaigui and Refaat Mohamed Mahfouz

S1. Comment

A new engineering strategy aimed at building very cohesive frameworks based on oxyanion subnetworks in which the organic molecules are strongly anchored thanks to different interactions (electrostatic, H-bonds, Van der Waals). These interactions are all important in the construction of atomic arrangement but short and multiple hydrogen-bonds observed in these frameworks appear to be the most exciting since they have been recognized as the steering force responsible for the formation of special networks (Katayev *et al.*, 2006). The oxoanions are good hydrogen bond acceptors, that's why they have been employed in the purification, extraction and detection techniques of dangerous pollutants (Ray *et al.*, 2003; Ray *et al.*, 2002; Rodrigues *et al.*, 2009). The 2-amino-3-nitropyridine molecule has a dual nature because of its donor and acceptor groups. It can be protonated and thus serve as a hydrogen bond donor and electrostatic attractive element and also serve as a hydrogen bond acceptor which is especially useful for the binding of oxoanions. In this paper, we will account on the crystal engineering of 2-amino-3-nitropyridinium perrhenate, $(C_5H_6N_3O_2)^+$, ReO_4^- (I).

The asymmetric unit of (I) consists of one perrhenate anion (ReO_4^-) and one organic cation $(C_5H_6N_3O_2)^+$ (Fig. 1).

The atomic arrangement of this salt is an organized dispersion of organic cations and inorganic anions which form alternate corrugated layers (Fig. 2). This projection shows too the extensive network of H-bonds, $N-H\cdots O$ and $C-H\cdots O$ between cation and anion and $C-H\cdots O$ between cations (Table 1). These interactions constitute a key factor as well as electrostatic interaction in the stabilization of this structure. The nitropyridinium cations form chains running parallel to the [101/2] direction. The $C-H\cdots O$ interactions have the same H-bonds geometric parameters as the $N-H\cdots O$ ones which may also consolidate the cohesion of this structure. The neighbour nitropyridinium cations, are linked to form one-dimensional chains via $C3-H3\cdots O5$ H-bonds (see Table 1 for symmetry codes) with $C\cdots O$ distance of 2.44 Å. Such chains of 2-amino-3-nitropyridinium are also observed in the related structure of 2 A3NPClO4 (Toumi Akriche *et al.*, 2010). In this structure, the $(C_5H_6N_3O_2)^{tm}$ chains connect the discrete ReO_4^- anions through $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds in all directions to develop a three-dimensional network. It's worth noticing that the particular behaviour of hydrogen of nitrogen atoms which establish bi- and trifurcated H-bonds, that well explains the weak values of the corresponding angles spreading between 123 and 141°.

The ReO_4^- anion have an expected but slightly distorted tetrahedral geometry around Re atom with the $Re-O$ bond lengths ranging from 1.665 (7) to 1.726 (6) Å and the $O-Re-O$ bond angles ranging from 107.4 (4) to 113.4 (4)°. The average $Re-O$ bond distances and $O-Re-O$ bond angles are 1.701 Å and 109.45°, respectively, confirming a tetrahedral configuration, similar to other studied perrhenates (Ray *et al.*, 2003; Ray *et al.*, 2002). Nevertheless, the calculated average values of the distortion indices (Baur *et al.*, 1974) corresponding to the different angles and distances in the independent ReO_4 tetrahedron ($DI(Re-O) = 0.011$, $DI(O-Re-O) = 0.017$, and $DI(O-O) = 0.013$) show an above distortion of the $O-O$ distances compared to $Re-O$ distances. The same feature is observed in ClO_4 tetrahedron

of the related structure of 2-amino-3-nitropyridinium perchlorate (Toumi Akriche *et al.*, 2010). However, the distortion indices observed in 2-amino-3-nitropyridinium phosphate and selenate structures show an above distortion of the X—O (X = P and Se) distances compared to O—O distances (Akriche *et al.*, 2000; Akriche *et al.*, 2009), that well explain the distortion of XO₄ tetrahedra (X = P and Se) in which the P and Se atoms are displaced of 0.114 to 0.065 Å from gravity center of XO₄. The ReO₄ tetrahedron is thus described by a regular oxygen atoms arrangement with the rhenium atom slightly shifted from gravity center of ReO₄ (0.042 Å).

As expected, the pyridinium ring of 2-amino-3-nitropyridinium cation is nearly planar, with maximum deviation from planarity equal to 0.021 (5) Å. The dihedral angle between the planes of the NO₂ group and the pyridinium ring is close to 4.25 (9)° indicating a deformation of the NO₂ group since the oxygen atoms of this later are the seat of various types of inter- and intramolecular hydrogen bonds. The geometrical characteristics of the (I) organic cation are normal and comparable to that observed for the same species in other structure (Akriche *et al.*, 2000; Toumi Akriche *et al.*, 2010; Akriche *et al.*, 2009).

S2. Experimental

An aqueous solution (10 ml) of NH₄ReO₄ (0.27 g; 1 mmol) is added drop by drop under stirring to an ethanolic solution (5 ml) of 2-amino-3-nitropyridine (0,139 g; 1 mmol) in the presence of HCL (1 M, 1 ml). Yellow solution was left in air for a week until yellow prisms of (I) were deposited on the wall of the beaker.

S3. Refinement

All H atoms attached to C and N atoms were fixed geometrically and treated as riding, with C—H = 0.93 Å and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$.

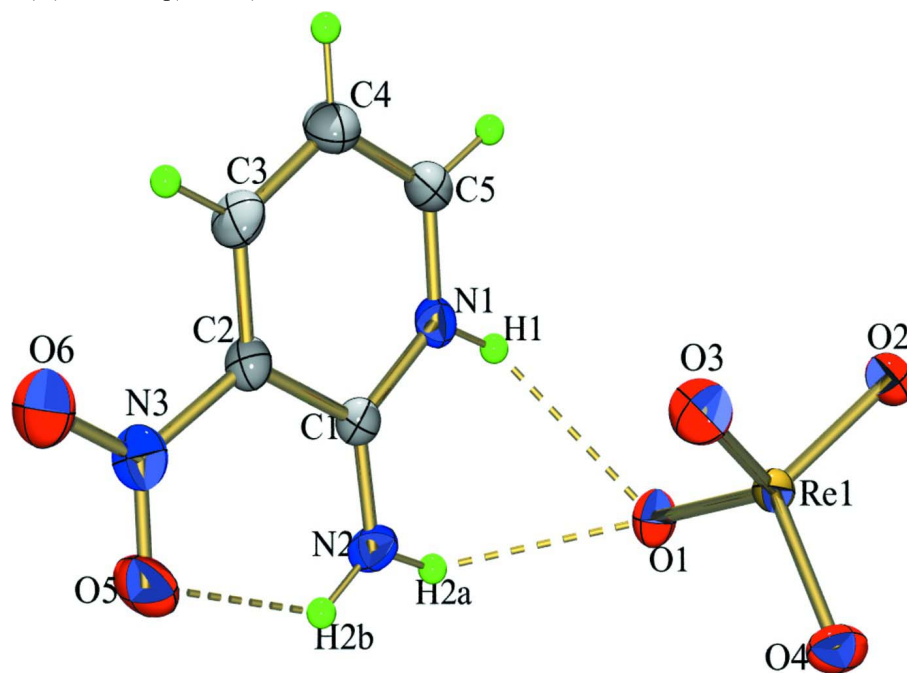


Figure 1

A view of (I) with displacement ellipsoids drawn at the 30% probability level. Hydrogen bonds are represented as dashed lines.

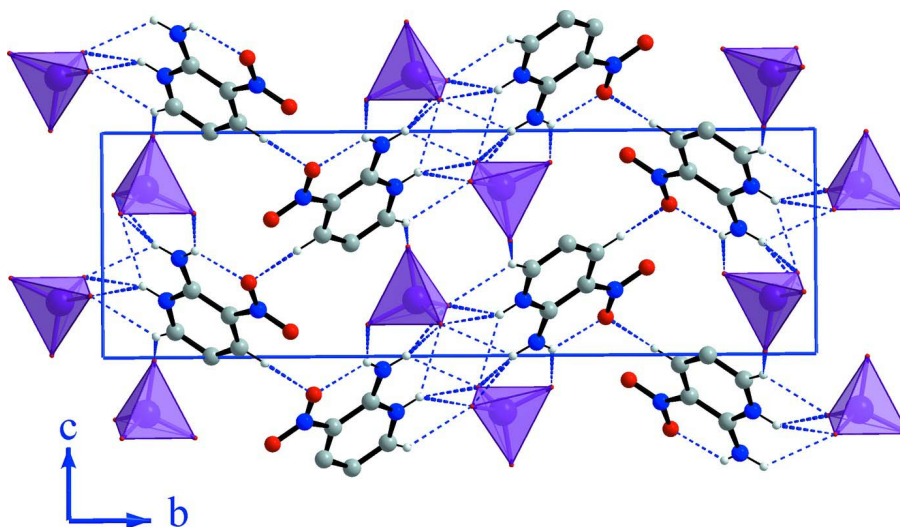


Figure 2

Projection of (I) along the a axis. The H-atoms not involved in H-bonding are omitted.

2-Amino-3-nitropyridinium perrhenate

Crystal data

$(\text{C}_5\text{H}_6\text{N}_3\text{O}_2)[\text{ReO}_4]$

$M_r = 390.33$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 6.235\ (3)\ \text{\AA}$

$b = 22.030\ (2)\ \text{\AA}$

$c = 7.840\ (6)\ \text{\AA}$

$\beta = 117.52\ (5)^\circ$

$V = 955.0\ (9)\ \text{\AA}^3$

$Z = 4$

$F(000) = 720$

$D_x = 2.715\ \text{Mg m}^{-3}$

Ag $K\alpha$ radiation, $\lambda = 0.56087\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 9\text{--}11^\circ$

$\mu = 6.86\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, yellow

$0.50 \times 0.40 \times 0.30\ \text{mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: Enraf–Nonius FR590

Graphite monochromator
non-profiled ω scans

Absorption correction: multi-scan
(Blessing, 1995)

$T_{\min} = 0.054$, $T_{\max} = 0.134$

7565 measured reflections

4682 independent reflections

3532 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -10 \rightarrow 10$

$k = -36 \rightarrow 0$

$l = -12 \rightarrow 13$

2 standard reflections every 120 min

intensity decay: 4%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.111$

$S = 1.07$

4682 reflections

137 parameters

24 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 2.5911P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.037$$

$$\Delta\rho_{\max} = 2.71 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -2.35 \text{ e } \text{Å}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.033 (2)

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.

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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Re1	0.71309 (5)	0.940210 (14)	0.25037 (4)	0.03320 (12)
O1	0.5590 (13)	0.9742 (3)	0.3597 (10)	0.0450 (14)
O2	0.9536 (13)	0.9832 (4)	0.2759 (11)	0.0544 (17)
O3	0.8207 (16)	0.8717 (4)	0.3586 (14)	0.062 (2)
O4	0.5164 (14)	0.9265 (4)	0.0220 (10)	0.0568 (19)
O5	0.2048 (17)	0.7952 (4)	0.6686 (16)	0.073 (2)
O6	0.453 (2)	0.7369 (5)	0.8873 (17)	0.088 (3)
N1	0.7550 (13)	0.9105 (4)	0.7469 (10)	0.0400 (14)
H1	0.7366	0.9443	0.6867	0.048*
N2	0.3526 (15)	0.8922 (3)	0.5588 (11)	0.0427 (15)
H2A	0.3378	0.9264	0.5019	0.051*
H2B	0.2288	0.8690	0.5260	0.051*
N3	0.4105 (19)	0.7821 (4)	0.7905 (14)	0.053 (2)
C1	0.5584 (15)	0.8757 (3)	0.6920 (11)	0.0338 (13)
C2	0.6059 (16)	0.8218 (4)	0.8141 (13)	0.0386 (14)
C3	0.8316 (19)	0.8088 (4)	0.9565 (15)	0.050 (2)
H3	0.8578	0.7733	1.0280	0.060*
C4	1.0226 (19)	0.8481 (6)	0.9954 (18)	0.058 (3)
H4	1.1769	0.8402	1.0937	0.070*
C5	0.9753 (18)	0.8982 (5)	0.8848 (15)	0.050 (2)
H5	1.1009	0.9248	0.9059	0.060*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.03010 (15)	0.03753 (17)	0.03126 (16)	−0.00110 (11)	0.01359 (11)	−0.00198 (11)
O1	0.057 (4)	0.041 (3)	0.045 (3)	−0.001 (3)	0.030 (3)	−0.002 (3)
O2	0.040 (3)	0.067 (5)	0.055 (4)	−0.007 (3)	0.022 (3)	0.008 (3)
O3	0.062 (5)	0.046 (4)	0.076 (6)	0.010 (3)	0.030 (4)	0.017 (4)
O4	0.044 (4)	0.078 (5)	0.039 (3)	0.001 (3)	0.012 (3)	−0.019 (3)
O5	0.057 (5)	0.057 (5)	0.090 (7)	−0.021 (4)	0.021 (4)	0.005 (5)

O6	0.090 (7)	0.059 (6)	0.103 (8)	-0.012 (5)	0.034 (6)	0.036 (5)
N1	0.041 (3)	0.037 (3)	0.046 (4)	-0.001 (2)	0.023 (3)	0.006 (3)
N2	0.046 (4)	0.035 (3)	0.037 (3)	-0.001 (3)	0.010 (3)	0.006 (3)
N3	0.064 (5)	0.031 (3)	0.064 (5)	-0.004 (3)	0.029 (4)	0.003 (3)
C1	0.039 (3)	0.028 (3)	0.034 (3)	-0.001 (2)	0.017 (3)	-0.003 (2)
C2	0.044 (4)	0.028 (3)	0.046 (4)	0.003 (3)	0.023 (3)	0.002 (3)
C3	0.054 (5)	0.038 (4)	0.057 (5)	0.014 (3)	0.024 (4)	0.017 (4)
C4	0.041 (4)	0.062 (6)	0.066 (6)	0.009 (4)	0.021 (4)	0.016 (5)
C5	0.040 (4)	0.057 (5)	0.052 (5)	-0.001 (4)	0.020 (4)	0.008 (4)

Geometric parameters (Å, °)

Re1—O1	1.726 (6)	C2—C3	1.363 (13)
Re1—O2	1.706 (7)	C2—N3	1.441 (12)
Re1—O3	1.708 (8)	C2—C1	1.466 (11)
Re1—O4	1.665 (7)	O5—N3	1.228 (14)
N1—C5	1.325 (12)	N3—O6	1.206 (12)
N1—C1	1.338 (11)	C3—C4	1.387 (16)
N1—H1	0.8600	C3—H3	0.9300
N2—C1	1.277 (11)	C5—C4	1.350 (15)
N2—H2A	0.8600	C5—H5	0.9300
N2—H2B	0.8600	C4—H4	0.9300
O4—Re1—O2	113.4 (4)	N2—C1—N1	121.7 (8)
O4—Re1—O3	107.4 (4)	N2—C1—C2	126.0 (8)
O2—Re1—O3	108.1 (4)	N1—C1—C2	112.1 (7)
O4—Re1—O1	108.1 (4)	C3—C2—N3	118.0 (8)
O2—Re1—O1	111.2 (4)	C3—C2—C1	121.8 (8)
O3—Re1—O1	108.5 (4)	N3—C2—C1	120.3 (8)
C5—N1—C1	126.5 (8)	C2—C3—C4	120.3 (9)
C5—N1—H1	116.8	C2—C3—H3	119.9
C1—N1—H1	116.8	C4—C3—H3	119.9
C1—N2—H2A	120.0	C5—C4—C3	117.3 (10)
C1—N2—H2B	120.0	C5—C4—H4	121.3
H2A—N2—H2B	120.0	C3—C4—H4	121.3
O6—N3—O5	122.0 (10)	N1—C5—C4	121.9 (10)
O6—N3—C2	119.7 (10)	N1—C5—H5	119.1
O5—N3—C2	118.3 (8)	C4—C5—H5	119.1
C3—C2—N3—O6	-4.7 (15)	C2—C3—C4—C5	-1.3 (17)
C1—C2—N3—O6	177.5 (10)	C5—N1—C1—N2	179.0 (9)
C3—C2—N3—O5	176.6 (10)	C5—N1—C1—C2	4.7 (12)
C1—C2—N3—O5	-1.2 (14)	C3—C2—C1—N2	-178.3 (9)
N3—C2—C3—C4	-174.9 (10)	N3—C2—C1—N2	-0.6 (13)
C1—C2—C3—C4	2.9 (15)	C3—C2—C1—N1	-4.3 (12)
C1—N1—C5—C4	-3.5 (17)	N3—C2—C1—N1	173.5 (8)
N1—C5—C4—C3	1.4 (18)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···O1	0.86	2.37	3.041 (10)	135
N1—H1···O2 ⁱ	0.86	2.42	3.018 (10)	128
N1—H1···O1 ⁱⁱ	0.86	2.48	3.077 (11)	128
N2—H2A···O1	0.86	2.38	3.036 (10)	133
N2—H2A···O1 ⁱⁱ	0.86	2.40	3.010 (10)	129
N2—H2A···O2 ⁱⁱⁱ	0.86	2.55	3.168 (11)	129
N2—H2B···O5	0.86	2.02	2.624 (11)	127
N2—H2B···O3 ⁱⁱⁱ	0.86	2.26	2.976 (12)	141
C3—H3···O5 ^{iv}	0.93	2.44	3.138 (12)	132
C5—H5···O4 ^v	0.93	2.32	3.094 (13)	141
C5—H5···O2 ⁱ	0.93	2.41	3.020 (13)	123

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