2-Amino-3-nitropyridinium perrhenate

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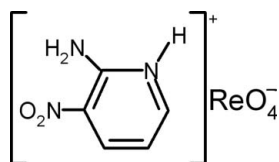Correspondence e-mail: toumiakriche@yahoo.fr

In the title molecular salt, $(C_5H_6N_3O_2)[ReO_4]$, the cations and tetrahedral anions are linked by trifurcated N—H$\cdots$(O,O,O) and bifurcated N—H$\cdots$(O,O) hydrogen bonds, as well as weak C—H$\cdots$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

$(C_5H_6N_3O_2)[ReO_4]$	V = 955.0 (9) Å^3
M_r = 390.33	Z = 4
Monoclinic, $P2_1/c$	Ag $K\alpha$ radiation
a = 6.235 (3) Å	λ = 0.56087 Å
b = 22.030 (2) Å	μ = 6.86 mm^{-1}
c = 7.840 (6) Å	T = 293 K
β = 117.52 (5)°	0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	4682 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	3532 reflections with $I > 2\sigma(I)$
T_{min} = 0.054, T_{max} = 0.134	R_{int} = 0.027
7565 measured reflections	2 standard reflections every 120 min intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040	24 restraints
$wR(F^2)$ = 0.111	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 2.71 e Å^{-3}
4682 reflections	$\Delta\rho_{min}$ = −2.35 e Å^{-3}
137 parameters	

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

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supplementary materials

2-Amino-3-nitropyridinium perrhenate

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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-nitropyridininium 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 oganic cations and inorganic anions which form alternate corrugated layers (Fig. 2). This projection shows too the extensive network of H-bonds, N—H···O and C—H···O between cation and anion and C—H···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···O interactions have the same H-bonds geometric parameters as the N—H···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···O5 H-bonds (see Table 1 for symmetry codes) with C···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 $(C_5H_6N_3O_2)^{+n}$ chains connect the discrete ReO_4^- anions through N—H···O and C—H···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

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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 XO_4 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 XO_4. The ReO_4 tetrahedron is thus described by a regular oxygen atoms arrangement with the rhenium atom slightly shifted from gravity center of ReO_4 (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 diedral angle between the planes of the NO_2 group and the pyridinium ring is close to 4.25 (9)° indicating a deformation of the NO_2 group since the oxygen atoms of this later are the seat of various types of inter-and intramolecular hydrogen bonds. The geometrical charcteristics 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).

Experimental

An aqueous solution (10 ml) of NH_4ReO_4 (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.

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 $U_{iso}(H) = 1.2Ueq(C \text{ or } N)$.
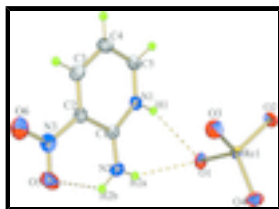
Figures

Fig. 1. A view of (I) with displacement ellipsoids drawn at the 30% probability level. Hydrogen bonds are represented as dashed lines.

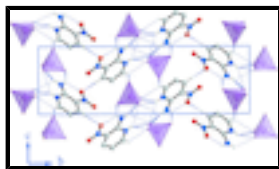Fig. 2. Projection of (I) along the *a* axis. The H-atoms not involved in H-bonding are omitted.

2-Amino-3-nitropyridinium perrhenate

Crystal data

$(C_5H_6N_3O_2)[ReO_4]$	$F(000) = 720$
$M_r = 390.33$	$D_x = 2.715$ Mg m^{-3}
Monoclinic, $P2_1/c$	Ag $K\alpha$ radiation, $\lambda = 0.56087$ Å
Hall symbol: -P 2ybc	Cell parameters from 25 reflections

$a = 6.235$ (3) Å	$\theta = 9–11°$
$b = 22.030$ (2) Å	$\mu = 6.86$ mm^{-1}
$c = 7.840$ (6) Å	$T = 293$ K
$\beta = 117.52$ (5)°	Prism, yellow
$V = 955.0$ (9) Å^3	$0.50 \times 0.40 \times 0.30$ mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	3532 reflections with $I > 2\sigma(I)$
Radiation source: Enraf–Nonius FR590	$R_{int} = 0.027$
graphite	$\theta_{max} = 28.0°$, $\theta_{min} = 2.4°$
non–profiled ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (Blessing, 1995)	$k = -36 \rightarrow 0$
$T_{min} = 0.054$, $T_{max} = 0.134$	$l = -12 \rightarrow 13$
7565 measured reflections	2 standard reflections every 120 min
4682 independent reflections	intensity decay: 4%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 2.5911P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.037$
4682 reflections	$\Delta\rho_{max} = 2.71$ e Å^{-3}
137 parameters	$\Delta\rho_{min} = -2.35$ e Å^{-3}
24 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	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, convention-al 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 ($Å^2$)

	x	y	z	U_{iso}*/U_{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, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
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.

Fig. 1

Fig. 2