# metal-organic compounds

# 2-Amino-5-nitropyridinium tetraoxidorhenate(VII) monohydrate

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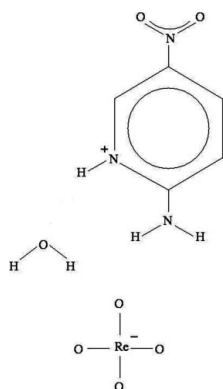
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All the residues of the title compound, $(C_5H_6N_3O_2)[ReO_4]\cdot H_2O$, are located on general crystallographic positions. The 2-amino-5-nitropyridinium cation has a typical planar conformation with one of the nitro O atoms −0.058 (5) Å out of plane; the amine H atoms are also a little out of the main ring plane towards the opposite side of the aforementioned O atom [by 0.02 (4) and 0.04 (4) Å]. The perrhenate anion is nearly ideally tetrahedral. Three distinct N—H⋯O hydrogen bonds give rise to $C(8)$ zigzag chains running along [100]. $R_4^4(12)$ rings involving the two hydrogen bonds in which the water molecules interact with the perrhenate anions are also present.

## Related literature

For the structural analyses of related 2-amino-5-nitropyridium salts and their potential application as non-linear optical materials, see: Masse & Zyss (1991); Puig-Molina *et al.* (1998); Aakeröy *et al.* (1998); Pecaut *et al.* (1993).

## Experimental

### Crystal data

$(C_5H_6N_3O_2)[ReO_4]\cdot H_2O$
$M_r = 408.34$
Monoclinic, $P2_1/c$
$a = 9.6914$ (3) Å
$b = 9.1357$ (3) Å
$c = 13.4636$ (4) Å
$\beta = 120.120$ (2)°

$V = 1031.08$ (6) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 11.81$ mm$^{-1}$
$T = 295$ K
$0.10 \times 0.06 \times 0.05$ mm

### Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.33$, $T_{max} = 0.55$

30757 measured reflections
2374 independent reflections
2175 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.033$
$S = 1.05$
2374 reflections
158 parameters
5 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.88$ e Å$^{-3}$
$\Delta\rho_{min} = -0.72$ e Å$^{-3}$

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| N1—H1⋯O3 | 0.86 | 1.93 | 2.738 (3) | 157 |
| N1—H1⋯O6[i] | 0.86 | 2.63 | 3.049 (4) | 112 |
| N2—H2A⋯O3 | 0.89 (3) | 2.33 (3) | 3.030 (4) | 135 (3) |
| N2—H2A⋯O4[ii] | 0.89 (3) | 2.65 (3) | 3.259 (4) | 127 (3) |
| N2—H2B⋯O5 | 0.89 (3) | 1.98 (3) | 2.846 (3) | 164 (3) |
| O3—H3A⋯O7[iii] | 0.89 (3) | 1.93 (3) | 2.802 (4) | 167 (3) |
| O3—H3B⋯O4[ii] | 0.89 (3) | 2.13 (3) | 2.862 (4) | 139 (3) |

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

## References

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# supporting information

## 2-Amino-5-nitropyridinium tetraoxidorhenate(VII) monohydrate

### V. H. Rodrigues, M. M. R. R. Costa, T. Dekola and E. de Matos Gomes

### S1. Experimental

Crystals of the title compound were obtained by slow evaporation from a water solution of analytical grade reagents on a 1:1 molar ratio. The reagents used were 2-amino-5-nitropyridine (99.5%) and a perrhenic acid solution (65–75% water 99.5%), both purchased from Aldrich.

### S2. Refinement

The structure was solved by direct methods using *SHELXS97*. All H atoms were first located on a difference Fourier map as a check for data quality; those bonded to C and N aromatic atoms were then placed at idealized positions and refined as riding [C—H=0.93 Å, N—H=0.86 Å, $U_{iso}(H)=1.2U_{eq}(C)$ and $U_{iso}(H)=1.2U_{eq}(N)$]. The coordinates of the amine H atoms were then refined only with the restraint that the N—H distance would be 0.89 Å within 0.2 Å. The positions of the H atoms belonging to the water molecule were also restrained so that the intramolecular O—H distance would be 0.89 Å and the H—H distance 1.40 Å, both within 0.02 Å, thus enforcing an acceptable geometry of the water molecule [$U_{iso}(H)=1.5U_{eq}(O)$].

Examination of the crystal structure with *PLATON* (Spek, 2009) showed that there are no solvent-accessible voids in the crystal lattice.
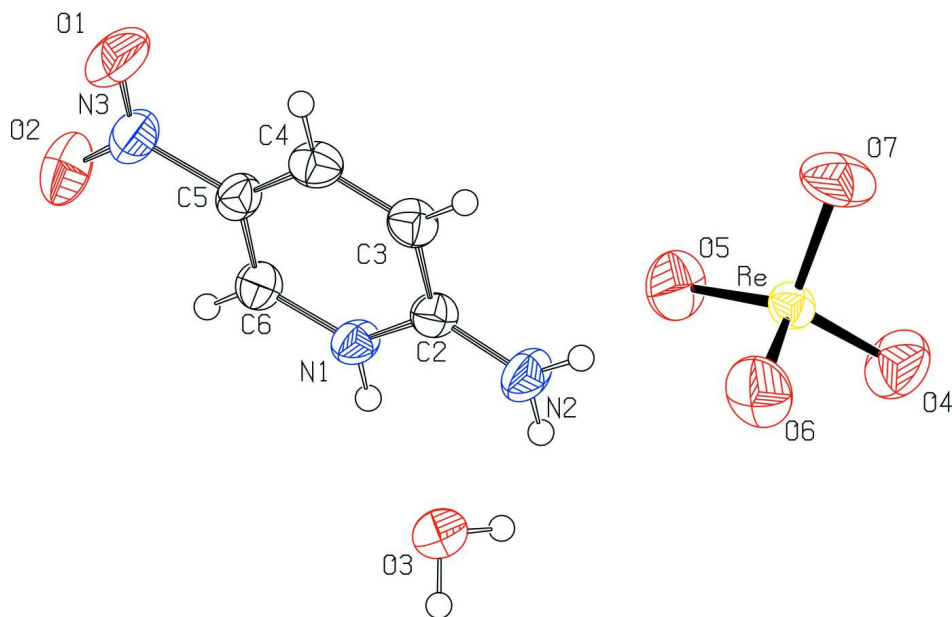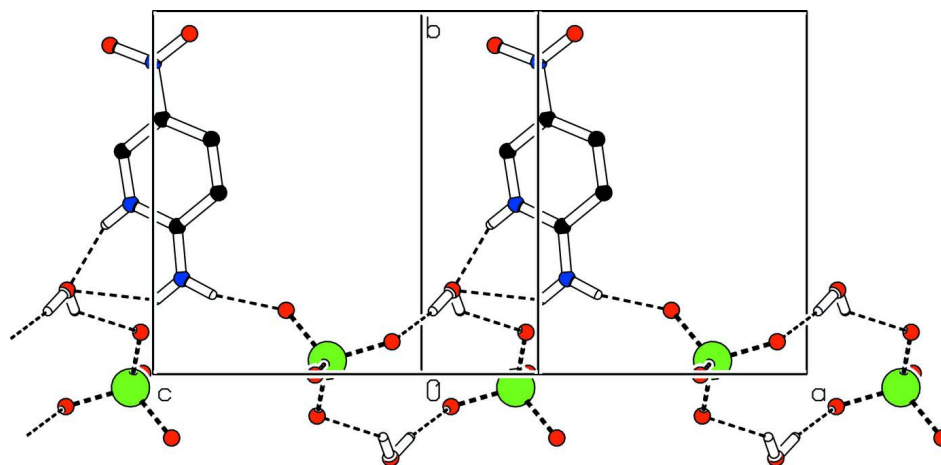
**Figure 1**

*ORTEPII* (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% level.



**Figure 2**

Zigzag chain running along the *a* axis. Small ring motifs made of a perrhenate anion and two water molecules are included in the chain. Hydrogen bonds are indicated with dashed lines.

**2-Amino-5-nitropyridinium tetraoxidorhenate(VII) monohydrate**

*Crystal data*

| | |
|---|---|
| $(C_5H_6N_3O_2)[ReO_4]\cdot H_2O$ | $F(000) = 760$ |
| $M_r = 408.34$ | $D_x = 2.631$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 9920 reflections |
| $a = 9.6914$ (3) Å | $\theta = 2.4–32.3°$ |
| $b = 9.1357$ (3) Å | $\mu = 11.81$ mm$^{-1}$ |
| $c = 13.4636$ (4) Å | $T = 295$ K |
| $\beta = 120.120$ (2)° | Prism, translucent colourless |
| $V = 1031.08$ (6) Å$^3$ | $0.10 \times 0.06 \times 0.05$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII diffractometer | 30757 measured reflections |
| Radiation source: fine-focus sealed tube | 2374 independent reflections |
| Graphite monochromator | 2175 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.030$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$ |
| $T_{min} = 0.33$, $T_{max} = 0.55$ | $h = -12 \rightarrow 12$ |
| | $k = -11 \rightarrow 11$ |
| | $l = -17 \rightarrow 17$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | 5 restraints |
| Least-squares matrix: full | Primary atom site location: structure-invariant direct methods |
| $R[F^2 > 2\sigma(F^2)] = 0.015$ | |
| $wR(F^2) = 0.033$ | Secondary atom site location: difference Fourier map |
| $S = 1.05$ | |
| 2374 reflections | Hydrogen site location: inferred from neighbouring sites |
| 158 parameters | |

| | |
|---|---|
| H atoms treated by a mixture of independent and constrained refinement | $\Delta\rho_{max} = 0.88$ e Å$^{-3}$ |
| $w = 1/[\sigma^2(F_o^2) + (0.0122P)^2 + 1.4451P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $\Delta\rho_{min} = -0.72$ e Å$^{-3}$ |
| | Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| $(\Delta/\sigma)_{max} = 0.001$ | Extinction coefficient: 0.00774 (16) |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.2958 (3) | 0.4684 (3) | 0.0719 (2) | 0.0338 (5) |
| H1 | 0.2145 | 0.4119 | 0.0493 | 0.041* |
| C2 | 0.4404 (3) | 0.4063 (3) | 0.1067 (2) | 0.0315 (6) |
| N2 | 0.4512 (3) | 0.2632 (3) | 0.1047 (3) | 0.0434 (6) |
| H2A | 0.367 (3) | 0.204 (3) | 0.080 (3) | 0.052* |
| H2B | 0.543 (2) | 0.219 (4) | 0.124 (3) | 0.052* |
| C3 | 0.5736 (3) | 0.4998 (3) | 0.1440 (3) | 0.0352 (6) |
| H3 | 0.6741 | 0.4605 | 0.1684 | 0.042* |
| C4 | 0.5549 (3) | 0.6463 (3) | 0.1442 (2) | 0.0362 (6) |
| H4 | 0.6420 | 0.7086 | 0.1688 | 0.043* |
| C5 | 0.4020 (3) | 0.7029 (3) | 0.1067 (2) | 0.0332 (6) |
| N3 | 0.3785 (4) | 0.8592 (3) | 0.1068 (2) | 0.0437 (6) |
| O1 | 0.4946 (4) | 0.9377 (3) | 0.1387 (3) | 0.0717 (9) |
| O2 | 0.2459 (3) | 0.9055 (3) | 0.0781 (3) | 0.0632 (7) |
| C6 | 0.2737 (3) | 0.6133 (3) | 0.0712 (2) | 0.0336 (6) |
| H6 | 0.1728 | 0.6517 | 0.0469 | 0.040* |
| O3 | 0.1012 (3) | 0.2314 (2) | 0.0301 (2) | 0.0538 (6) |
| H3A | 0.083 (5) | 0.174 (3) | 0.076 (2) | 0.081* |
| H3B | 0.079 (5) | 0.174 (3) | −0.030 (2) | 0.081* |
| Re | 0.905465 (12) | 0.037384 (13) | 0.215124 (10) | 0.03195 (6) |
| O4 | 0.8222 (3) | −0.1153 (3) | 0.1338 (2) | 0.0680 (7) |
| O5 | 0.7677 (3) | 0.1758 (3) | 0.1707 (3) | 0.0632 (7) |
| O6 | 0.9713 (4) | −0.0024 (3) | 0.3551 (2) | 0.0674 (8) |
| O7 | 1.0618 (3) | 0.0893 (3) | 0.1987 (3) | 0.0664 (8) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0264 (11) | 0.0290 (12) | 0.0452 (15) | −0.0007 (9) | 0.0174 (11) | 0.0031 (11) |
| C2 | 0.0289 (12) | 0.0319 (14) | 0.0329 (15) | 0.0032 (11) | 0.0150 (11) | 0.0054 (12) |
| N2 | 0.0375 (13) | 0.0281 (13) | 0.0627 (18) | 0.0052 (11) | 0.0237 (14) | 0.0057 (13) |

| C3 | 0.0262 (13) | 0.0400 (16) | 0.0369 (16) | 0.0004 (11) | 0.0142 (12) | 0.0010 (13) |
|---|---|---|---|---|---|---|
| C4 | 0.0312 (13) | 0.0411 (17) | 0.0341 (16) | −0.0090 (12) | 0.0147 (12) | −0.0035 (13) |
| C5 | 0.0417 (15) | 0.0277 (14) | 0.0296 (15) | 0.0020 (12) | 0.0175 (12) | 0.0023 (12) |
| N3 | 0.0597 (17) | 0.0299 (13) | 0.0415 (15) | 0.0009 (12) | 0.0254 (13) | 0.0003 (11) |
| O1 | 0.080 (2) | 0.0345 (13) | 0.108 (3) | −0.0181 (13) | 0.0530 (19) | −0.0083 (14) |
| O2 | 0.0674 (17) | 0.0398 (14) | 0.0761 (19) | 0.0152 (13) | 0.0313 (15) | 0.0003 (13) |
| C6 | 0.0320 (13) | 0.0329 (15) | 0.0351 (15) | 0.0054 (12) | 0.0161 (12) | 0.0046 (13) |
| O3 | 0.0643 (16) | 0.0382 (13) | 0.0750 (19) | −0.0090 (12) | 0.0471 (15) | −0.0043 (13) |
| Re | 0.02646 (7) | 0.03566 (8) | 0.03418 (8) | 0.00296 (4) | 0.01554 (5) | 0.00215 (5) |
| O4 | 0.0773 (19) | 0.0537 (16) | 0.0667 (18) | −0.0151 (14) | 0.0315 (15) | −0.0156 (14) |
| O5 | 0.0447 (13) | 0.0583 (16) | 0.0843 (19) | 0.0226 (12) | 0.0307 (13) | 0.0131 (15) |
| O6 | 0.085 (2) | 0.0780 (19) | 0.0394 (15) | 0.0150 (16) | 0.0313 (14) | 0.0090 (13) |
| O7 | 0.0398 (13) | 0.083 (2) | 0.086 (2) | 0.0057 (13) | 0.0389 (14) | 0.0225 (17) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C6 | 1.341 (4) | C5—C6 | 1.360 (4) |
| N1—C2 | 1.358 (3) | C5—N3 | 1.446 (4) |
| N1—H1 | 0.8600 | N3—O1 | 1.216 (4) |
| C2—N2 | 1.313 (4) | N3—O2 | 1.217 (4) |
| C2—C3 | 1.413 (4) | C6—H6 | 0.9300 |
| N2—H2A | 0.89 (3) | O3—H3A | 0.89 (3) |
| N2—H2B | 0.89 (3) | O3—H3B | 0.89 (3) |
| C3—C4 | 1.351 (4) | Re—O6 | 1.698 (3) |
| C3—H3 | 0.9300 | Re—O7 | 1.704 (2) |
| C4—C5 | 1.402 (4) | Re—O4 | 1.705 (3) |
| C4—H4 | 0.9300 | Re—O5 | 1.714 (2) |
| | | | |
| C6—N1—C2 | 123.2 (2) | C6—C5—N3 | 118.6 (3) |
| C6—N1—H1 | 118.4 | C4—C5—N3 | 120.1 (3) |
| C2—N1—H1 | 118.4 | O1—N3—O2 | 123.3 (3) |
| N2—C2—N1 | 119.2 (3) | O1—N3—C5 | 117.7 (3) |
| N2—C2—C3 | 122.8 (3) | O2—N3—C5 | 119.0 (3) |
| N1—C2—C3 | 118.0 (3) | N1—C6—C5 | 118.5 (2) |
| C2—N2—H2A | 123 (2) | N1—C6—H6 | 120.7 |
| C2—N2—H2B | 122 (2) | C5—C6—H6 | 120.7 |
| H2A—N2—H2B | 115 (3) | H3A—O3—H3B | 104 (3) |
| C4—C3—C2 | 120.0 (3) | O6—Re—O7 | 109.89 (15) |
| C4—C3—H3 | 120.0 | O6—Re—O4 | 109.31 (15) |
| C2—C3—H3 | 120.0 | O7—Re—O4 | 108.01 (15) |
| C3—C4—C5 | 118.9 (3) | O6—Re—O5 | 109.77 (14) |
| C3—C4—H4 | 120.6 | O7—Re—O5 | 109.69 (13) |
| C5—C4—H4 | 120.6 | O4—Re—O5 | 110.15 (14) |
| C6—C5—C4 | 121.3 (3) | | |
| | | | |
| C6—N1—C2—N2 | 179.9 (3) | C4—C5—N3—O1 | 1.0 (4) |
| C6—N1—C2—C3 | 0.1 (4) | C6—C5—N3—O2 | 1.9 (4) |
| N2—C2—C3—C4 | −179.9 (3) | C4—C5—N3—O2 | −177.2 (3) |

| N1—C2—C3—C4 | −0.1 (4) | C2—N1—C6—C5 | 0.1 (4) |
| C2—C3—C4—C5 | −0.2 (4) | C4—C5—C6—N1 | −0.4 (4) |
| C3—C4—C5—C6 | 0.4 (4) | N3—C5—C6—N1 | −179.5 (3) |
| C3—C4—C5—N3 | 179.5 (3) | N1—C2—N2—H2A | 1 (3) |
| C6—C5—N3—O1 | −179.9 (3) | C3—C2—N2—H2B | −3 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
| --- | --- | --- | --- | --- |
| N1—H1···O3 | 0.86 | 1.93 | 2.738 (3) | 157 |
| N1—H1···O6[i] | 0.86 | 2.63 | 3.049 (4) | 112 |
| N2—H2*A*···O3 | 0.89 (3) | 2.33 (3) | 3.030 (4) | 135 (3) |
| N2—H2*A*···O4[ii] | 0.89 (3) | 2.65 (3) | 3.259 (4) | 127 (3) |
| N2—H2*B*···O5 | 0.89 (3) | 1.98 (3) | 2.846 (3) | 164 (3) |
| O3—H3*A*···O7[iii] | 0.89 (3) | 1.93 (3) | 2.802 (4) | 167 (3) |
| O3—H3*B*···O4[ii] | 0.89 (3) | 2.13 (3) | 2.862 (4) | 139 (3) |

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