

2-(2-Pyridyl)pyridinium perchlorate, redetermined at 120 K: complex hydrogen-bonded sheets

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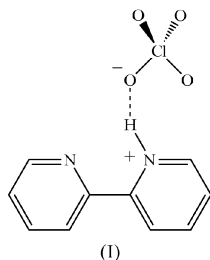
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In the title compound, $C_{10}H_9N_2^+ \cdot ClO_4^-$, the ions are linked into complex sheets by the combination of one $N-H \cdots O$ and four independent $C-H \cdots O$ hydrogen bonds.

Comment

The structure of the title compound, (I), was determined many years ago (Lipkowski *et al.*, 1976); using diffraction data collected at ambient temperature, the structure was refined only to $R = 0.072$. We have now redetermined this structure using diffraction data collected at 120 K and report here a more precise determination, together with the interesting supramolecular structure of this compound. The space group and unit-cell dimensions confirm that the previous study and the present work involve the same phase.



The title compound (Fig. 1) is a salt, and in the selected asymmetric unit, the two ions are linked by an $N-H \cdots O$ hydrogen bond. In the cation, the dihedral angle between the two ring planes is $14.96(15)^\circ$, similar to the value of 16.6° reported previously for the ambient-temperature structure (Lipkowski *et al.*, 1976). In addition, there is a significant difference in the $C-N-C$ angles at the protonated atom N11 and the unprotonated atom N21 (Table 1). In the anion, the $Cl-O$ distance involving atom O1 is somewhat longer than the other $Cl-O$ distances, possibly reflecting some modest localization of the negative charge.

In addition to the $N-H \cdots O$ hydrogen bond, involving the more negative atom O1 as the acceptor, there are a number of independent $C-H \cdots O$ hydrogen bonds (Table 2). Although these all have fairly long $H \cdots O$ distances, they all appear to have some structural significance, including the effective tethering of the perchlorate anion, for which the anisotropic displacement parameters give no indication of significant libration, far less of the type of disorder for which this anion is notorious. Hence, we conclude that these interactions are significant. All of the hydrogen bonds involve donors in the protonated pyridinium ring, leading to more acidic $X-H$ bonds ($X = C$ or N), and all four O atoms of the anion act as acceptors, so precluding any significant librational motion for the anion.

The $C-H \cdots O$ hydrogen bond involving atom C16 as the donor reinforces the $N-H \cdots O$ hydrogen bond in linking together the two independent ions, so forming an $R_2^2(7)$ motif, and the combination of this and the interaction having atom C13 as the donor then generates by translation a $C_2^2(8)C_2^2(9)[R_2^2(7)]$ chain of rings running parallel to the $[10\bar{1}]$ direction (Fig. 2). The two hydrogen bonds having atoms C14 and C15 as the donors act co-operatively to form a zigzag chain of edge-fused rings running parallel to the $[20\bar{1}]$ direc-

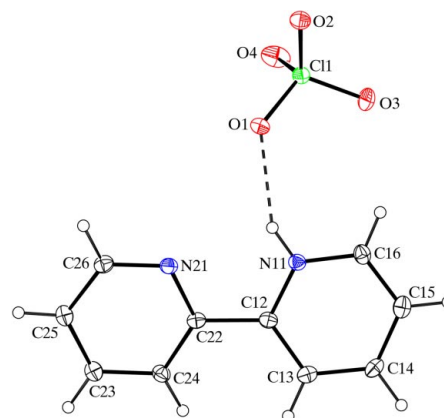


Figure 1

The independent components of compound (I), showing the atom-labelling scheme and the $N-H \cdots O$ hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

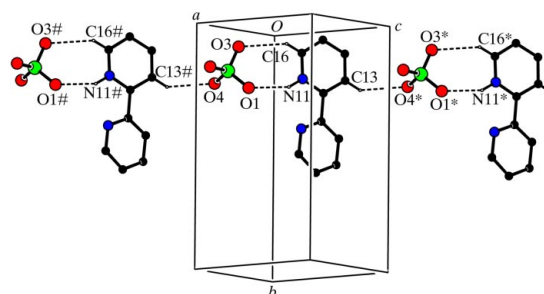
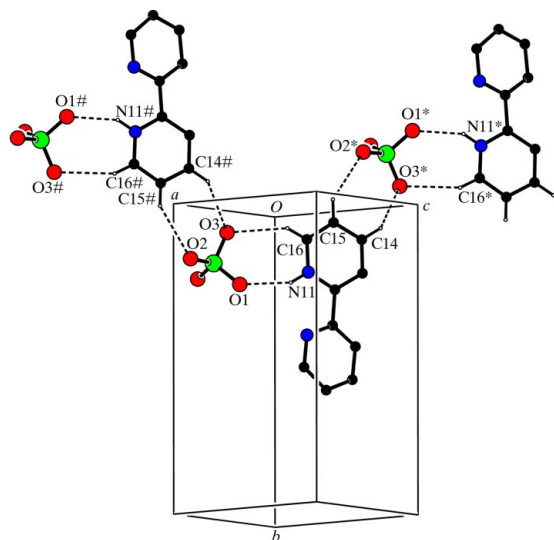


Figure 2

Part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of rings along $[10\bar{1}]$. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x-1, y, 1+z)$ and $(1+x, y, z-1)$, respectively.


Figure 3

Part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of rings along $[20\bar{1}]$. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x - 1, -y, \frac{1}{2} + z)$ and $(1 + x, -y, z - \frac{1}{2})$, respectively.

tion and generated by the c -glide plane at $y = 0$ (Fig. 3). The combination of the $[10\bar{1}]$ and $[20\bar{1}]$ chains then generates a complex (010) sheet.

Experimental

2,2'-Bipyridine (3.2 mmol) was dissolved in ethanol (25 ml) and perchloric acid (3.2 mmol) was then added dropwise. The reaction mixture was warmed in a water bath for 15 min and colourless crystals of (I) separated out on cooling (m.p. 441 K).

Crystal data

$C_{10}H_9N_2^+ \cdot ClO_4^-$
 $M_r = 256.64$
 Monoclinic, Pc
 $a = 5.958$ (4) Å
 $b = 12.854$ (4) Å
 $c = 7.060$ (11) Å
 $\beta = 100.26$ (7)°
 $V = 532.0$ (9) Å³
 $Z = 2$

$D_x = 1.602$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2313 reflections
 $\theta = 3.2$ – 27.5 °
 $\mu = 0.36$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.18 \times 0.12 \times 0.02$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.954$, $T_{\max} = 0.993$
 6904 measured reflections

2313 independent reflections
 2035 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 27.5$ °
 $h = -7 \rightarrow 7$
 $k = -16 \rightarrow 16$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.115$
 $S = 1.07$
 2313 reflections
 155 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.011P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³
 Absolute structure: Flack (1983), with 1086 Friedel pairs
 Flack parameter: 0.03 (16)

Table 1

Selected geometric parameters (Å, °).

C11—O1	1.452 (3)	C11—O3	1.439 (2)
C11—O2	1.433 (2)	C11—O4	1.438 (3)
C12—N11—C16	123.3 (3)	C22—N21—C26	117.0 (2)
N11—C12—C22—N21	-14.6 (4)	C13—C12—C22—N21	164.1 (3)
N11—C12—C22—C23	166.0 (3)	C13—C12—C22—C23	-15.3 (4)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11—H11 \cdots O1	0.88	2.11	2.902 (6)	150
C13—H13 \cdots O4 ⁱ	0.95	2.51	3.328 (7)	144
C14—H14 \cdots O3 ⁱⁱ	0.95	2.57	3.375 (7)	142
C15—H15 \cdots O2 ⁱⁱ	0.95	2.57	3.365 (6)	141
C16—H16 \cdots O3	0.95	2.52	3.289 (6)	139

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

The systematic absences permitted Pc and $P2/c$ as possible space groups; Pc was selected and confirmed by the subsequent analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 Å and N—H distances of 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The correct orientation of the structure with respect to the polar-axis directions (Jones, 1986) was determined by means of the Flack (1983) parameter.

Data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1853). Services for accessing these data are described at the back of the journal.

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