

2-(2-Pyridylamino)pyridinium perchlorate displaying a one-dimensional hydrogen-bonding supramolecular chain

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

Disorder in main residue

R factor = 0.069

wR factor = 0.199

Data-to-parameter ratio = 10.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_{10}\text{H}_{10}\text{N}_3^+\cdot\text{ClO}_4^-$, the cation adopts the normal *trans-trans* configuration and an approximately planar geometry. Hydrogen-bonding interactions between the cations and perchlorate anions extend this structure into a one-dimensional chain architecture.

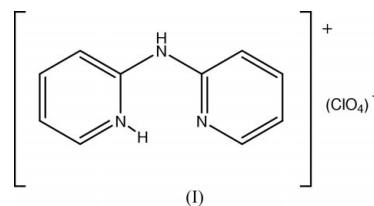
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Comment

Chelating ligands containing aromatic nitrogen heterocycles, such as the well known compounds 2,2'-bipyridine and 1,10-phenanthroline, have given a great impetus to coordination chemistry. Among them, bis(2-pyridyl)amine has attracted much interest in the formation of directly bonded linear chains of metal centers (Cotton *et al.*, 1997, 1998) or photoluminescent materials (Du & Zhao, 2004a). On the other hand, aromatic compounds of this type usually exhibit interesting proton-sponge properties (Du & Zhao, 2004b), *i.e.* represent a species that can act as proton acceptors through the formation of $\text{N}-\text{H}\cdots\text{Y}$ hydrogen bonds. Very recently, the crystal structure of the nitrate salt of protonated bis(2-pyridyl)amine was determined (Du & Zhao, 2004c). In the present contribution, we report the molecular and supramolecular structure of the perchlorate salt of protonated bis(2-pyridyl)amine, (I).



The crystal structure of (I) consists of a monoprotonated cation, $[\text{C}_{10}\text{H}_{10}\text{N}_3]^+$, and a perchlorate anion. The cation adopts the normal *trans-trans* configuration; all non-H atoms within the cation are almost coplanar and the mean deviation of any atom from the least-squares plane is 0.014 (6) Å. The dihedral angle between the pyridine and pyridyl rings is only 1.5 (5)°. Selected bond lengths and angles are listed in Table 1.

Analysis of the crystal packing of the title compound shows the existence of $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions, which connect the cation and perchlorate anions into a one-dimensional chain motif. As depicted in Fig. 1, within the monoprotonated cation, an intramolecular $\text{N1}-\text{H1A}\cdots\text{N3}$ hydrogen bond is observed. The protonated NH group also forms an intermolecular $\text{N1}-\text{H1A}\cdots\text{O2}^i$ (Table 2) hydrogen bond with the adjacent perchlorate anion. Additionally, the amide group is involved in an $\text{N2}-\text{H2A}\cdots\text{O4}$

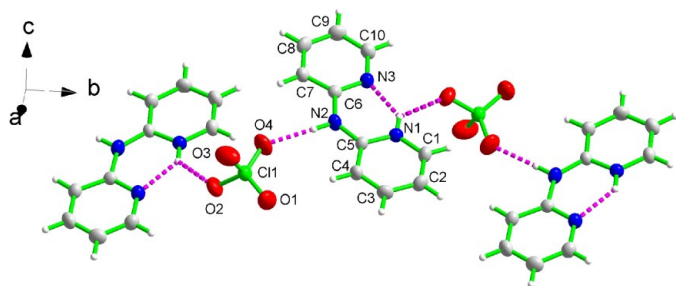


Figure 1
A view of the one-dimensional supramolecular chain formed *via* hydrogen-bonding interactions in (I), with displacement ellipsoids drawn at the 30% probability level. It should be noted that only one disorder component is shown for the anions.

hydrogen bond with the perchlorate anion. Thus the perchlorate anions bridge the cations to form a one-dimensional supramolecular chain *via* hydrogen bonds (Fig. 1). The relevant hydrogen-bonding geometric details are listed in Table 2; these values are in the normal range for such hydrogen-bonding interactions (Desiraju & Steiner, 1999). Examination of this structure with *PLATON* (Spek, 2003) shows that there are no solvent-accessible voids or significant π - π stacking interactions.

Experimental

Several drops of a dilute aqueous solution of HClO_4 were added to a solution of bis(2-pyridyl)amine in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$. After *ca* 10 min of mixing, the resulting clear solution was filtered and set aside, affording colorless lamellar single crystals of (I) suitable for X-ray diffraction within one week. Analysis calculated for the title compound: C 44.21, H 3.71, N 15.46%; found: C 44.07, H 3.99, N 15.39%. FT-IR (KBr pellet, cm^{-1}): 3074 (w), 2945 (w), 1665 (s), 1602 (s), 1561 (s), 1508 (m), 1483 (w), 1454 (s), 1427 (w), 1304 (w), 1244 (s), 1202 (w), 1146 (s), 1114 (s), 1087 (s), 1037 (s), 1030 (m), 1004 (w), 931 (w), 900 (w), 882 (w), 840 (w), 809 (w), 776 (s), 737 (w), 624 (m).

Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_3^+\cdot\text{ClO}_4^-$	$D_x = 1.522 \text{ Mg m}^{-3}$
$M_r = 271.66$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 925 reflections
$a = 8.527(3) \text{ \AA}$	$\theta = 2.7\text{--}21.4^\circ$
$b = 16.174(5) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$c = 8.753(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$\beta = 100.878(6)^\circ$	Plate, colorless
$V = 1185.5(7) \text{ \AA}^3$	$0.24 \times 0.20 \times 0.08 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	2033 independent reflections
φ and ω scans	1165 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2000)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.866$, $T_{\text{max}} = 0.970$	$\theta_{\text{max}} = 25.0^\circ$
4794 measured reflections	$h = -10 \rightarrow 7$
	$k = -14 \rightarrow 19$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.1137P)^2]$
$wR(F^2) = 0.200$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2033 reflections	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
200 parameters	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C5	1.347 (6)	N2—C6	1.388 (6)
N1—C1	1.349 (6)	N3—C6	1.316 (6)
N2—C5	1.338 (6)	N3—C10	1.341 (6)
C5—N1—C1	121.9 (4)	C6—N3—C10	118.1 (4)
C5—N2—C6	131.8 (4)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1A \cdots N3	0.86	1.96	2.623 (6)	133
N1—H1A \cdots O2 ⁱ	0.86	2.47	3.149 (5)	137
N2—H2A \cdots O4	0.86	1.94	2.785 (6)	166

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

Although all H atoms were visible in difference maps, they were finally placed at calculated positions (0.93 \AA for aromatic C—H and 0.86 \AA for N—H distances) and refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$. Although we have tried many times, the lamellar single crystals obtained were too thin for structure determination of better than modest precision. In the refinement, a disorder model of the perchlorate anion was used (two constraint components for four O atoms of the perchlorate anion have occupancy factors of 0.564 and 0.436, respectively); however, the O atoms still exhibit slightly larger displacement ellipsoids than usual.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL97*.

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