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Bis(2-pyridylmethyl)ammonium perchlorate

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Key indicators

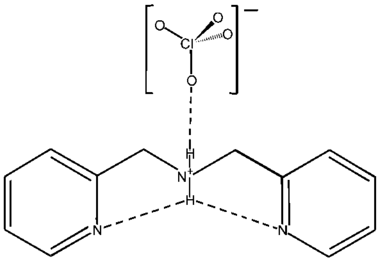
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.055
wR factor = 0.156
Data-to-parameter ratio = 9.8

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

The title compound, $C_{12}H_{14}N_3^+\cdot ClO_4^-$, crystallizes from a solution of bis(2-pyridylmethyl)amine and $HClO_4$ in water/DMF (3:1, *v*/*v*) with the secondary amine N atom protonated. The two pyridine arms of the ligand are held in a closed conformation through a strong bifurcated hydrogen bond from one of the ammonium H atoms. The ClO_4^- anion is also hydrogen bonded to the same H atom of the ammonium N atom, with an N···O distance of 2.899 (4) Å. The other ammonium H atom is hydrogen bonded to an O atom of a symmetry-related perchlorate anion.

Comment

Bis(2-pyridylmethyl)amine has been used as chelating ligand for several metal ions, as a single unit, or as two or more units bridged by other groups through the amine N atom (Gultneh *et al.*, 1999; Palaniandavar *et al.*, 1995). We report here the structure of the perchlorate salt, (I), of the protonated compound. Because the pK_a of the amine N atom (determined to be 7.3) is much higher than those of the pyridyl groups (pK_a of 2.26 and 1.12) (Romary *et al.*, 1967), the amine N atom is protonated, while the pyridyl N atoms are hydrogen bonded at longer distances. The N—H bond lengths were constrained to be 0.90 Å, with tetrahedral angles about the central amine N atom. The $N_{pyridyl}\cdots H$ distances are far longer [N1*A*···H1N 2.53 (1) and N1*A*···H2N 2.52 (1) Å; N1*B*···H1N 2.48 (1) and N1*B*···H2N 2.56 (1) Å]. Based on N—H···N angles, atom H1N forms a hydrogen bond with N1*B* [129 (1)°] and H2N with N1*A* [125 (1)°]. The perchlorate ion O atoms are involved in hydrogen bonds with the amine H atoms, with variable N—H···O perchlorate angles ranging from 130 (1) to 159 (1)°. The amine–pyridine N···N distances are 2.657 (3) and 2.649 (3) Å, while the intramolecular pyridine–pyridine N···N distance is 4.511 (3) Å. The average $N_{amine}–H\cdots N_{pyridyl}$ angle is 127 (15)°.



(I)

Experimental

The title compound was synthesized by the reaction, at ice temperature, of 2-picolyl chloride and 2-(aminomethyl)pyridine in basic aqueous solution by a literature method (Romary *et al.*, 1967)

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and was purified by vacuum distillation. On dissolving the yellow oil in DMF/H_2O (3/1) and adding aqueous $HClO_4$, the perchlorate salt of the monoprotonated compound crystallized out as clear yellow crystals.

Crystal data

$C_{12}H_{14}N_3^+ \cdot ClO_4^-$
$M_r = 299.71$
Orthorhombic, *Pbca*
$a = 11.3201$ (18) Å
$b = 14.422$ (2) Å
$c = 17.073$ (3) Å
$V = 2787.3$ (7) Å^3
$Z = 8$
$D_x = 1.428$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 11.6$–13.0°
$\mu = 0.29$ mm^{-1}
$T = 293$ (2) K
Plate, pale yellow
0.84 × 0.56 × 0.10 mm

Data collection

Siemens *P*4S diffractometer
$2\theta/\omega$ scans
Absorption correction: refdelf (*SHELXTL*; Sheldrick, 1997)
$T_{min} = 0.728$, $T_{max} = 0.971$
2448 measured reflections
2448 independent reflections
1676 reflections with $I > 2\sigma(I)$

$\theta_{max} = 25.0°$
$h = -13 \rightarrow 0$
$k = -17 \rightarrow 0$
$l = -20 \rightarrow 0$
3 standard reflections every 97 reflections intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.156$
$S = 1.03$
2448 reflections
250 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 2.1051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O3C^i	0.90	2.18	3.015 (17)	154
N—H1N···O2B^i	0.90	2.10	2.789 (10)	132
N—H1N···O3A^i	0.90	2.07	2.869 (7)	147
N—H2N···O1C	0.90	2.11	2.953 (18)	155
N—H2N···O1D	0.90	2.10	2.958 (19)	159
N—H2N···O2A	0.90	2.11	2.875 (9)	143
N—H2N···O1B	0.90	2.43	3.095 (13)	130

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

Molecule (I) crystallized in the orthorhombic system; space group Pbca was assumed from the systematic absences. H atoms were treated as riding atoms (C—H 0.93 and 0.97 Å; N—H 0.9 Å). The disordered perchlorate anion was modeled with four sets of four O atoms, each set restrained to tetrahedral geometry, and with the sum of their occupancies (0.471, 0.287, 0.145 and 0.097, respectively) constrained to be equal to one.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

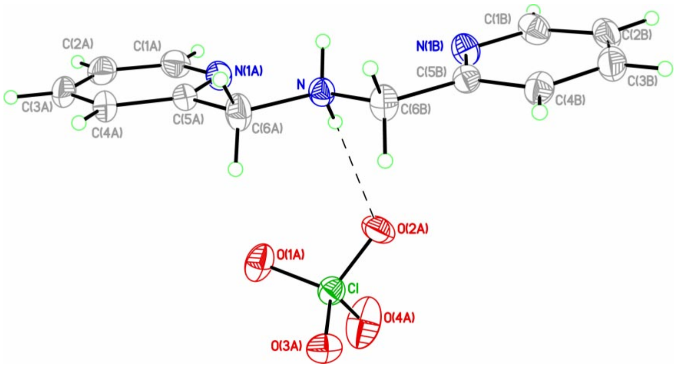

Figure 1
View of the ion pair of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size.

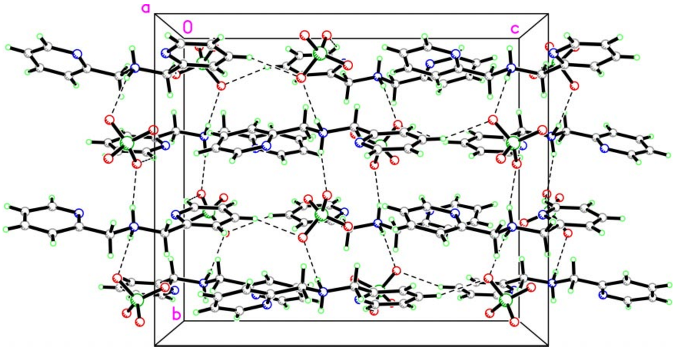

Figure 2
The molecular packing of (I), viewed along the *a* axis.

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