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Bis(2-pyridylethyl)ammonium perchlorate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.053
wR factor = 0.158
Data-to-parameter ratio = 14.3

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

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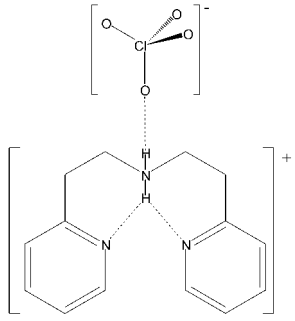
The title compound, $C_{14}H_{18}N_3^+\cdot ClO_4^-$, a perchlorate salt of the monoprotonated form of bis(2-pyridylethyl)amine, has a structure in which one of the two H atoms on the amine N atom forms hydrogen bonds to the two pyridyl N atoms in a chelating fashion, while the second H atom on the amine is also used in hydrogen bonding to a perchlorate O atom.

Comment

The tridentate ligand bis(2-pyridylethyl)amine (bpea) has been extensively used to synthesize transition metal complexes in modeling metalloenzyme active sites, due in part due to its similarity, in donor properties, to the biological donor, histidyl imidazole. Two or more units have been linked to produce ligands with the possibilities of forming multinuclear complexes. The groups of Brewer (Smieja *et al.*, 1991), Camus (Marsich *et al.*, 1998), Fenton (Adams *et al.*, 1996), Gultneh (Gultneh *et al.*, 1998), Holm (Lim & Holm, 1998), Hoskins (Hoskins & Whillans, 1975), Itoh (Itoh *et al.*, 2001, and references therein), Karlin (Itoh *et al.*, 2001, and references therein), Kitagawa (Itoh *et al.*, 2001, and references therein), Lippard (He *et al.*, 2000), Oshio (Oshio & Ichida, 1995), Reglier (Blain *et al.*, 2000), Toftlund (Schindler *et al.*, 2000) and Tomada (Iwaoka & Tomada, 1995) have used bpea as a chelating ligand for several metal ions, either as a single unit or as two or more units bridged by other moieties through the amine N atom. We report here the structure of the perchlorate salt of the monoprotonated form of this ligand.



(I)

The amine N atom, with a pK_a (8.95) higher than the two pyridine N atoms (3.40 and 4.08), is protonated. The amine N—H bond distances were constrained to be 0.90 Å, with tetrahedral angles about the N atom. One of the two H atoms on the amine N atom forms intramolecular hydrogen bonds with the two pyridyl N atoms (2.15 and 2.21 Å), folding the ligand in a chelate fashion. This is in marked contrast to the related bis(pyridyl)amine salt, bis(2-pyridylmethyl)-ammonium perchlorate (Butcher *et al.*, 2002), where the

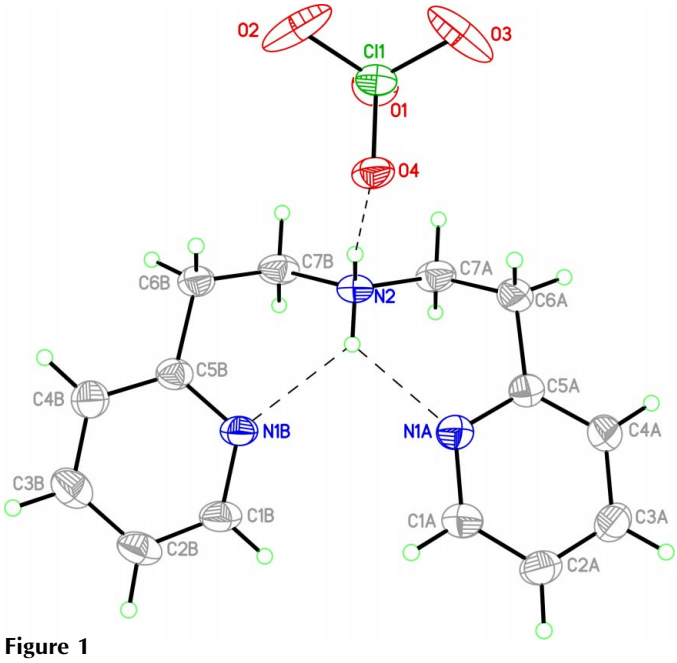


Figure 1
View of the ion pair of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size. For the disordered perchlorate anion, only the major component is shown.

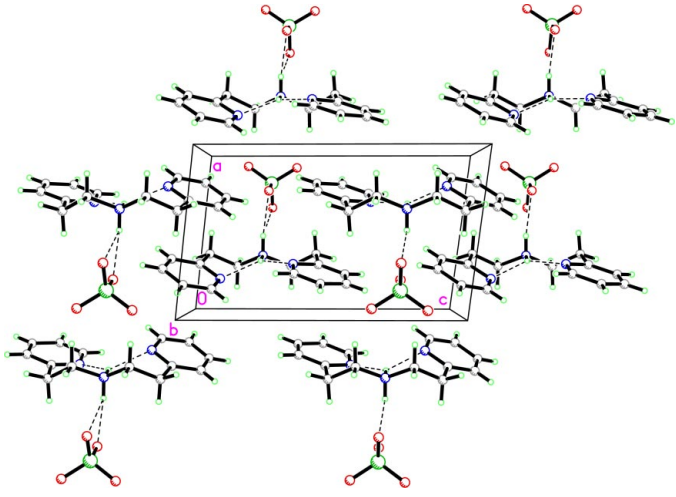


Figure 2
The molecular packing of the title compound viewed down the *b* axis. For the disordered perchlorate anion, only the major component is shown.

methylene bridge between the amine N atom and the pyridine ring is not sufficiently flexible to permit the ammonium H atoms to form intramolecular hydrogen bonds with the pyridyl N atoms. The other H atom on the amine N atom forms hydrogen bonds with perchlorate O atoms, in which the H···O distances range from 2.11 to 2.58 Å. The $N_{amine}\cdots N_{pyridyl}$ distances are 2.810 (3) and 2.846 (3) Å and the N_{amine}—H···$N_{pyridyl}$ angles are 130 and 127°. The $N_{amine}\cdots O$ distances range from 3.005 (3) to 3.178 (3) Å, while the N_{amine}—H···O angles range from 124 to 172°. In the crystal, face-to-face stacking of the pyridyl rings along the *a* axis is observed (Fig. 2). The *B* ring (C1*B*–C5*B*/N1*B*) makes a more parallel stack than the *A* ring (C1*A*–C5*A*/N1*A*). In the stacks, the centroids of the *B* ring and the *B* rings of the symmetry-related molecules at $(-x, 1-y, -z)$ and $(1-x, 1-y, -z)$ are separated by distances of 3.680 (2) and 3.738 (2) Å, respectively, while those of the *A* ring and the *A* rings of the symmetry-related molecules at $(-x, 1-y, 1-z)$ and $(1-x, 1-y, 1-z)$ are separated by 3.785 (2) and 3.769 (2) Å, respectively.

Experimental

The title compound was obtained, as colorless crystals, by acidification of a solution of the free base, bis[2-(2-pyridyl)ethyl]amine in a DMF–H_2O (3/1) mixture with a 0.1 *M* aqueous solution of $HClO_4$.

Crystal data

$C_{14}H_{18}N_3^+\cdot ClO_4^-$
M_r = 327.76
Triclinic, $P\overline{1}$
a = 7.4093 (11) Å
b = 9.0987 (11) Å
c = 12.161 (2) Å
α = 88.477 (13)°
β = 82.986 (17)°
γ = 80.079 (12)°
V = 801.5 (2) Å^3
Z = 2
D_x = 1.358 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 53 reflections
θ = 4.9–12.5°
μ = 0.26 mm^{-1}
T = 293 (2) K
Needle, colorless
0.80 × 0.34 × 0.17 mm

Data collection

Siemens *P4S* diffractometer
ω scans
Absorption correction: refined from Δ*F* (*SHELXTL*; Sheldrick, 1997)
T_{min} = 0.754, T_{max} = 0.862
3967 measured reflections
3681 independent reflections
2318 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.5°
h = −9 → 0
k = −11 → 11
l = −15 → 15
3 standard reflections
every 97 reflections
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.158
S = 1.02
3681 reflections
257 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.1918P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.030
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H0*A*···O4*B*	0.90	2.26	3.151 (6)	170
N2—H0*A*···O4	0.90	2.11	3.005 (3)	172
N2—H0*A*···O2*A*	0.90	2.35	3.200 (6)	158
N2—H0*A*···O1	0.90	2.58	3.178 (3)	124
N2—H0*B*···N1*A*	0.90	2.15	2.810 (3)	130
N2—H0*B*···N1*B*	0.90	2.21	2.846 (3)	127

All H atoms were fixed geometrically and allowed to ride on their parent atoms (C—H 0.93 and 0.97 Å, and N—H = 0.90 Å). The disordered perchlorate anion was modeled with three tetrahedral sets of O atoms, with the sum of their occupancies (0.590, 0.203 and 0.207) constrained to be equal to one.

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

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