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4-(Ammoniomethyl)pyridinium dichloride

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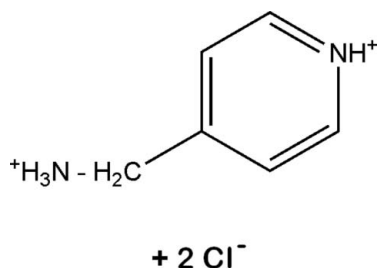
Received 10 October 2008; accepted 21 October 2008

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.030; data-to-parameter ratio = 17.7.

The title compound, $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{Cl}^-$, contains a network of 4-(ammoniomethyl)pyridinium cations and chloride anions which are interconnected by $\text{N}-\text{H} \cdots \text{Cl}$ hydrogen bonds. The crystal packing is also influenced by intermolecular $\pi-\pi$ stacking interactions between identical antiparallel organic cations with a face-to-face distance of *ca* 3.52 Å.

Related literature

For common applications of this type of complex, see: Schmidtchen & Berger, (1997); Pajewski *et al.* (2004); Sessler *et al.* (2003); Ilioudis *et al.* (2000). For structure cohesion, see: Bernstein *et al.*, (1995); Jin *et al.*, 2005. For discussion of the C–N–C angle, see: Krygowski *et al.* (2005). For bond-length data, see: Oueslati *et al.* (2006).



Experimental

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{Cl}^-$
 $M_r = 181.06$
 Triclinic, $\overline{P}1$
 $a = 7.257$ (2) Å
 $b = 7.339$ (3) Å
 $c = 8.752$ (1) Å
 $\alpha = 79.14$ (3)°
 $\beta = 79.94$ (4)°

$\gamma = 70.19$ (3)°
 $V = 412.9$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.71$ mm⁻¹
 $T = 293$ K
 $0.16 \times 0.15 \times 0.12$ mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Absorption correction: none
 3311 measured reflections
 1995 independent reflections

1670 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$
 2 standard reflections
 every 400 reflections
 intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.030$
 $S = 1.06$
 1609 reflections

91 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{Cl1}^i$	0.83	2.36	3.084 (2)	146
$\text{N2}-\text{H8} \cdots \text{Cl1}$	0.89	2.28	3.160 (3)	171
$\text{N2}-\text{H9} \cdots \text{Cl2}^{ii}$	0.90	2.23	3.126 (2)	173
$\text{N2}-\text{H10} \cdots \text{Cl2}^{iii}$	0.89	2.37	3.190 (2)	152

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

Data collection: *CAD-4 EXPRESS* (Straver, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *RC93* (Watkin *et al.*, 1994); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2217).

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supporting information

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4-(Ammoniomethyl)pyridinium dichloride

Meher El Glaoui, Riadh Kefi, Olfa Amri, Erwann Jeanneau and Cherif Ben Nasr

S1. Comment

The coordination chemistry of anions was the starting point for the development of new compounds having many practical and potential applications in various fields, such as supramolecular chemistry (Schmidtchen and Berger, 1997) and biochemical processes (Pajewski *et al.*, 2004). Moreover, halide anions have been successfully used to assemble double-helical motifs of various molecules containing aromatic groups, with π -stacking interactions within the helices (Sessler *et al.*, 2003). These anions can be useful for such applications because of the high flexibility of their coordination (Ilioudis *et al.*, 2000). Here, a new member of this family, the title compound ($C_6H_{10}Cl_2N_2$), is presented, which has been obtained during our studies of the preparation of new organic hydrochloride compounds. As shown in Fig. 1, to ensure charge balance the organic species is doubly protonated at N1 and N2. Thus, the structure consists essentially of an 4-(ammoniomethyl)pyridinium cations and two Cl⁻ anions, associated in a hydrogen-bonded network. The Cl⁻ anions and the antiparallel pair of organic cations associate each other *via* hydrogen-bonding interactions to construct a convoluted hydrogen-bonded chain network which runs along the [111] direction at $b = 1/2$ (Fig. 3). This chain is made up by a four-membered donor-acceptor ring, involving two Cl atoms, fused along the N—H \cdots Cl hydrogen bond (Fig. 2). These intermolecular hydrogen bonds generate edge-fused [$R_2^4(8)$ and $R_2^4(20)$] motifs (Bernstein *et al.*, 1995). When viewed in perspective, the molecules chains have a marked zigzag structure and somewhat resembles a helix. As can be seen in Fig.2, the neighbouring pyridinyl rings run parallel in opposite directions and stack each other by turns in a face-to-face mode. The nearest centroid-centroid distance is 3.52 Å, less than 3.8 Å, a usually accepted maximum value for π - π interactions (Jin *et al.*, 2005). An examination of the organic moiety geometrical features shows that the atoms building the pyridinyl ring have a good coplanarity and they form a conjugated plane with average deviation of 0.005 Å). The mean value of C—C and N—C bond lengths are 1.381 (2) and 1.332 (2) Å which are between that of a single bond and a double bond and agree with those in the literature (Oueslati *et al.*, 2006). However, it is worth noticing that the C—N—C angles of pyridine are very sensitive to protonation (Krygowski *et al.*, 2005). A pyridinium cation always possesses an expanded angle of C—N—C in comparison with the parent pyridine. The C1—N1—C5 angle [122.3 (2) °] is consistent with the type of pyridinium cation. In fact, the protonation of the nitrogen atom N1 decreases its electronegativity; hence the corresponding C—N—C angles becomes larger.

S2. Experimental

An aqueous 1M HCl solution and 4-(amminomethyl)pyridine in a 2:1 molar ratio were mixed and dissolved in sufficient ethanol. Crystals of (I) grew as the ethanol evaporated at 293 K over the course of a few days.

S3. Refinement

The refinement was carried out with $I\sigma(I) > 3$ and a $\sin\theta/\lambda > 0.01$ to get rid of the reflections in the vicinity of the beamstop. The refinement was thus carried out using 1609 reflections (out of the 1995 independent ones). The R value reported

corresponds to the recomputed value with a 2σ cutoff (SHELX like).

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 and O—H = 0.82 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

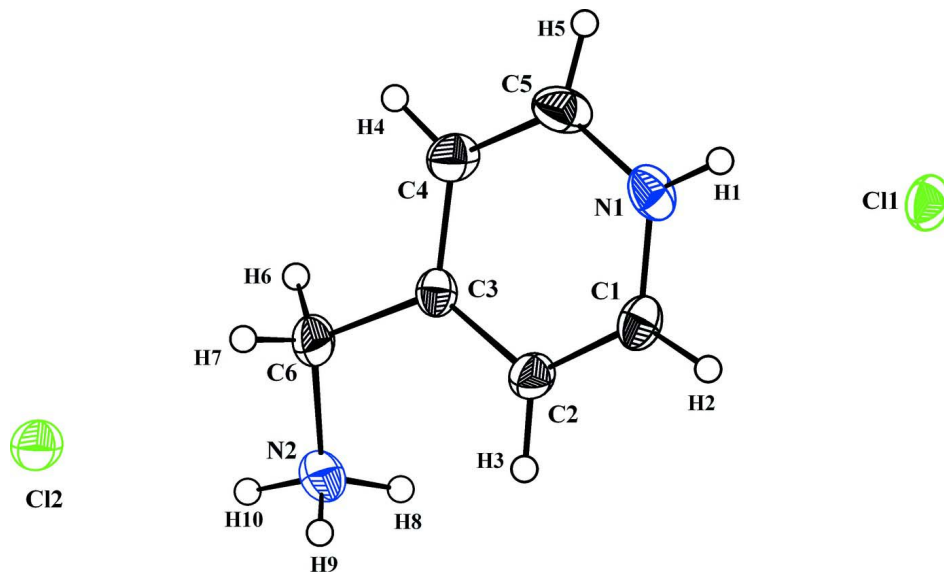


Figure 1

A view of (I), showing 40% probability displacement ellipsoids and arbitrary spheres for the H atoms.

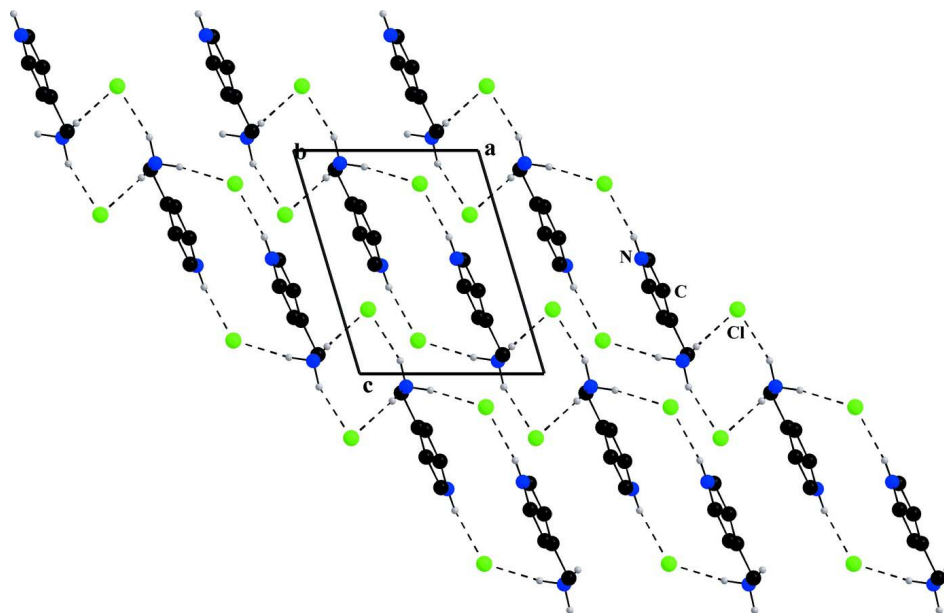
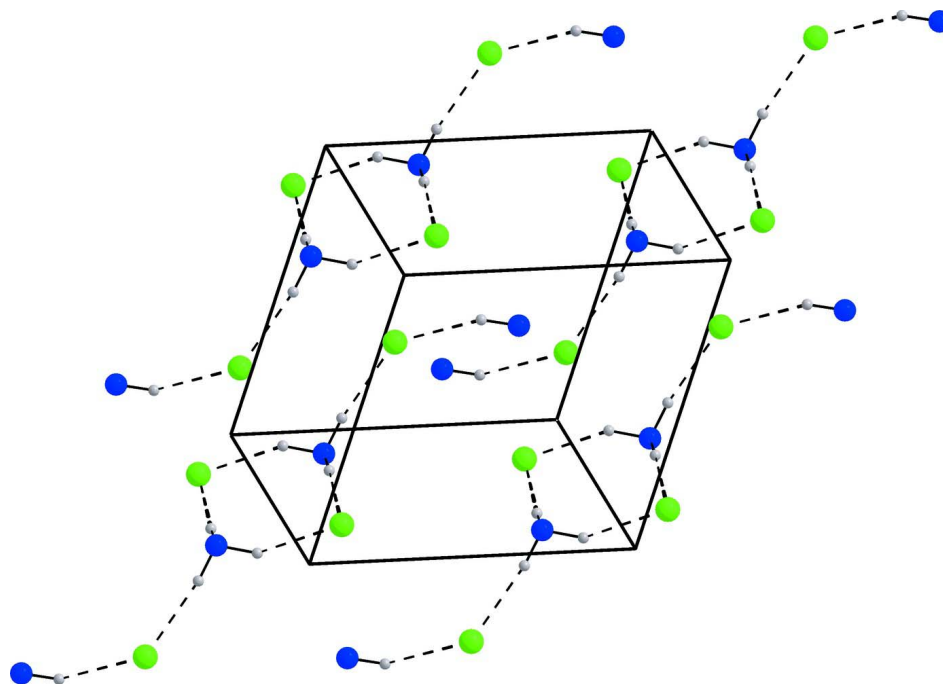


Figure 2

Crystal structure of $\text{C}_6\text{H}_{10}\text{Cl}_2\text{N}_2$ viewed along b axis showing that the molecules crystallize in a ring motif.

**Figure 3**

Perspective view of (I) showing four chains across the unit cell at $b = 1/2$ in the $[111]$ direction

4-(Ammoniomethyl)pyridinium dichloride

Crystal data

$C_6H_{10}N_2^{2+} \cdot 2Cl^-$

$M_r = 181.06$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.257\ (2)\ \text{\AA}$

$b = 7.339\ (3)\ \text{\AA}$

$c = 8.752\ (1)\ \text{\AA}$

$\alpha = 79.14\ (3)^\circ$

$\beta = 70.94\ (4)^\circ$

$\gamma = 70.19\ (3)^\circ$

$V = 412.9\ (2)\ \text{\AA}^3$

$Z = 2$

$F(000) = 188$

$D_x = 1.456\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 9\text{--}11^\circ$

$\mu = 0.71\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.16 \times 0.15 \times 0.12\ \text{mm}$

Data collection

Enraf–Nonius CAD-4

diffractometer

Graphite monochromator

$\omega/2\theta$ scans

3311 measured reflections

1995 independent reflections

1670 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 2.5^\circ$

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -5 \rightarrow 11$

2 standard reflections every 400 reflections

intensity decay: 4%

Refinement

Refinement on F

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.030$

$S = 1.06$

1609 reflections

91 parameters

0 restraints

Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained

[weight] = 1.0/[A₀*T₀(x) + A₁*T₁(x) ... +
 A_{n-1}]*T_{n-1}(x)]
 where A_i are the Chebychev coefficients listed
 below and x = F / Fmax W = [weight] *
 [1-(deltaF/6*sigmaF)²]² A_i are: 0.823 0.257
 0.531
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.29 e Å⁻³
 Δρ_{min} = -0.20 e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U _{iso} */U _{eq}
C11	0.36975 (6)	0.70916 (5)	0.85091 (4)	0.0357
C12	0.85118 (6)	0.60355 (5)	0.28807 (4)	0.0385
H1	0.6965	1.2683	0.3992	0.0408*
H2	0.7426	0.9613	0.4009	0.0420*
H3	0.7984	0.7600	0.6294	0.0385*
H4	0.7325	1.2354	0.8318	0.0427*
H5	0.6824	1.4162	0.5939	0.0458*
H6	0.7155	0.9365	1.0028	0.0427*
H7	0.9427	0.8393	0.9126	0.0426*
H8	0.6516	0.6757	0.9274	0.0509*
H9	0.8719	0.5860	0.8743	0.0510*
H10	0.7711	0.6183	1.0429	0.0511*
N1	0.71013 (19)	1.20012 (18)	0.48454 (13)	0.0347
N2	0.76974 (19)	0.66782 (17)	0.94222 (14)	0.0340
C1	0.7421 (2)	1.0097 (2)	0.49055 (16)	0.0330
C2	0.7738 (2)	0.8922 (2)	0.62759 (16)	0.0309
C3	0.76881 (19)	0.97525 (19)	0.76000 (15)	0.0263
C4	0.7352 (2)	1.1743 (2)	0.74770 (16)	0.0350
C5	0.7057 (3)	1.2852 (2)	0.60805 (18)	0.0401
C6	0.8048 (2)	0.8595 (2)	0.91467 (16)	0.0334

Atomic displacement parameters (Å²)

	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
C11	0.0459 (2)	0.04261 (19)	0.02508 (16)	-0.01833 (15)	-0.01593 (13)	0.00223 (12)
C12	0.0537 (2)	0.03529 (18)	0.02893 (17)	-0.01461 (15)	-0.01409 (14)	-0.00186 (13)
N1	0.0390 (6)	0.0379 (6)	0.0203 (5)	-0.0065 (5)	-0.0087 (4)	0.0048 (4)
N2	0.0397 (6)	0.0337 (6)	0.0276 (5)	-0.0107 (5)	-0.0136 (5)	0.0062 (4)
C1	0.0371 (7)	0.0430 (8)	0.0218 (6)	-0.0148 (6)	-0.0090 (5)	-0.0036 (5)
C2	0.0393 (7)	0.0304 (6)	0.0266 (6)	-0.0136 (5)	-0.0116 (5)	-0.0011 (5)
C3	0.0265 (6)	0.0314 (6)	0.0214 (5)	-0.0101 (5)	-0.0071 (4)	0.0003 (5)
C4	0.0487 (8)	0.0343 (7)	0.0220 (6)	-0.0146 (6)	-0.0070 (6)	-0.0037 (5)
C5	0.0564 (9)	0.0271 (7)	0.0287 (7)	-0.0076 (6)	-0.0074 (6)	-0.0010 (5)
C6	0.0420 (7)	0.0359 (7)	0.0262 (6)	-0.0129 (6)	-0.0162 (5)	0.0024 (5)

Geometric parameters (Å, °)

H3—C2	0.923	H9—N2	0.899
H2—C1	0.919	N1—C1	1.331 (2)
H5—C5	0.909	N1—C5	1.333 (2)
H8—N2	0.890	N2—C6	1.4750 (19)
H7—C6	0.955	C6—C3	1.5065 (18)
H6—C6	0.961	C1—C2	1.3750 (19)
H1—N1	0.831	C3—C2	1.3929 (18)
H4—C4	0.923	C3—C4	1.386 (2)
H10—N2	0.890	C5—C4	1.371 (2)
H1—N1—C1	118.7	H2—C1—N1	117.8
H1—N1—C5	118.6	H2—C1—C2	122.2
C1—N1—C5	122.62 (12)	N1—C1—C2	120.03 (13)
H9—N2—H8	109.1	C6—C3—C2	123.50 (12)
H9—N2—H10	107.4	C6—C3—C4	117.95 (12)
H8—N2—H10	109.7	C2—C3—C4	118.52 (12)
H9—N2—C6	109.8	H5—C5—N1	116.9
H8—N2—C6	111.9	H5—C5—C4	123.6
H10—N2—C6	108.9	N1—C5—C4	119.51 (14)
N2—C6—H6	109.7	C3—C2—C1	119.26 (13)
N2—C6—H7	108.0	C3—C2—H3	121.6
H6—C6—H7	108.4	C1—C2—H3	119.2
N2—C6—C3	114.31 (11)	C3—C4—H4	121.5
H6—C6—C3	107.3	C3—C4—C5	120.05 (13)
H7—C6—C3	108.9	H4—C4—C5	118.4

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...C11 ⁱ	0.83	2.36	3.084 (2)	146
N2—H8...C11	0.89	2.28	3.160 (3)	171
N2—H9...C12 ⁱⁱ	0.90	2.23	3.126 (2)	173
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