organic compounds

4-(Ammoniomethyl)pyridinium dichloride

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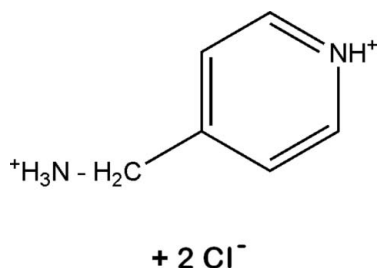
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The title compound, $C_6H_{10}N_2^{2+} \cdot 2Cl^-$, contains a network of 4-(ammoniomethyl)pyridinium cations and chloride anions which are interconnected by N—H⋯Cl hydrogen bonds. The crystal packing is also influenced by intermolecular π–π stacking 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

$C_6H_{10}N_2^{2+} \cdot 2Cl^-$	γ = 70.19 (3)°
M_r = 181.06	V = 412.9 (2) Å³
Triclinic, $P\bar{1}$	Z = 2
a = 7.257 (2) Å	Mo $K\alpha$ radiation
b = 7.339 (3) Å	μ = 0.71 mm⁻¹
c = 8.752 (1) Å	T = 293 K
α = 79.14 (3)°	0.16 × 0.15 × 0.12 mm
β = 70.94 (4)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	1670 reflections with $I > 2\sigma(I)$
Absorption correction: none	R_{int} = 0.014
3311 measured reflections	2 standard reflections
1995 independent reflections	every 400 reflections
	intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029	91 parameters
$wR(F^2)$ = 0.030	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 0.29 e Å⁻³
1609 reflections	$\Delta\rho_{min}$ = −0.20 e Å⁻³

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯Cl1[i]	0.83	2.36	3.084 (2)	146
N2—H8⋯Cl1	0.89	2.28	3.160 (3)	171
N2—H9⋯Cl2[ii]	0.90	2.23	3.126 (2)	173
N2—H10⋯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 materials

4-(Ammoniomethyl)pyridinium dichloride

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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···Cl hydrogen bond (Fig. 2). These intermolecular hydrogen bonds generate edge-fussed [$R_2^4(8)$ 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 acceptad 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.

Experimental

An aqueous 1*M* 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.

Refinement

The refinement was carried out with Iσ(I)>3 and a sinθ/λ>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).

supplementary materials

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 $U_{iso}(H)$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.
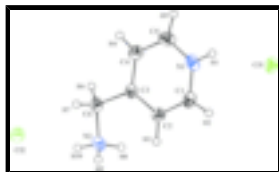
Figures

Fig. 1. A view of (I), showing 40% probability displacement ellipsoids and arbitrary spheres for the H atoms.
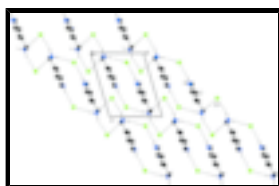

Fig. 2. Crystal structure of $C_6H_{10}Cl_2N_2$ viewed along b axis showing that the molecules crystallize in a ring motif.
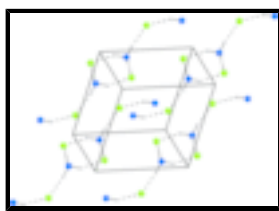

Fig. 3. Perspective view of (I) showing four chains across the unit cell at b = 1/2 in the [111] direction

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Crystal data

$C_6H_{10}N_2{}^{2+}\cdot 2Cl^-$	$Z = 2$
$M_r = 181.06$	$F_{000} = 188$
Triclinic, $P\bar{1}$	$D_x = 1.456$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.257$ (2) Å	Cell parameters from 25 reflections
$b = 7.339$ (3) Å	$\theta = 9–11°$
$c = 8.7520$ (10) Å	$\mu = 0.71$ mm^{-1}
$\alpha = 79.14$ (3)°	$T = 293$ K
$\beta = 70.94$ (4)°	Block, colorless
$\gamma = 70.19$ (3)°	$0.16 \times 0.15 \times 0.12$ mm
$V = 412.9$ (2) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 28.0°$
Monochromator: graphite	$\theta_{min} = 2.5°$

$T = 293$ K	$h = -9 \rightarrow 9$
$\omega/2\theta$ scans	$k = -9 \rightarrow 9$
Absorption correction: none	$l = -5 \rightarrow 11$
3311 measured reflections	2 standard reflections
1995 independent reflections	every 400 reflections
1670 reflections with $I > 2\sigma(I)$	intensity decay: 4%
$R_{int} = 0.014$	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
	$[weight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where A_i are the Chebychev coefficients listed below and $x = F/F$max W = $[weight] * [1-(deltaF/6*sigmaF)^2]^2$ A_i are: 0.823 0.257 0.531
$wR(F^2) = 0.030$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
1609 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
91 parameters	Extinction correction: None
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cl1	0.36975 (6)	0.70916 (5)	0.85091 (4)	0.0357
Cl2	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 (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0459 (2)	0.04261 (19)	0.02508 (16)	−0.01833 (15)	−0.01593 (13)	0.00223 (12)
Cl2	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, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1[i]	0.83	2.36	3.084 (2)	146
N2—H8···Cl1	0.89	2.28	3.160 (3)	171
N2—H9···Cl2[ii]	0.90	2.23	3.126 (2)	173

N2—H10···Cl2ⁱⁱⁱ   0.89   2.37   3.190 (2)   152
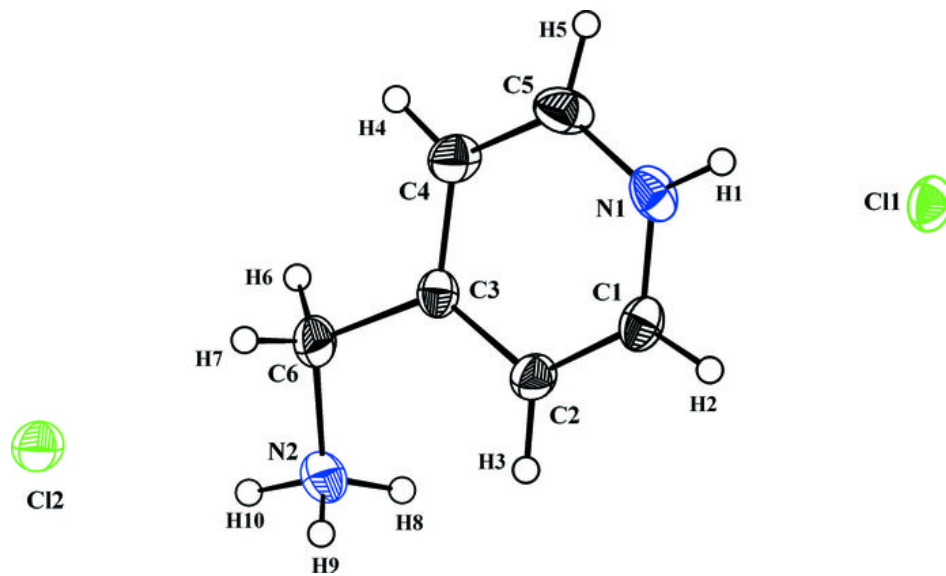
Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1; (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*, *y*, *z*+1.

Fig. 1

Fig. 2

Fig. 3