

3-Amino-6-chloropyridazinium chloride

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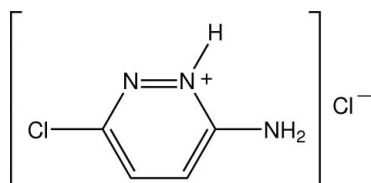
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.033; wR factor = 0.090; data-to-parameter ratio = 14.9.

In the title compound, $\text{C}_4\text{H}_5\text{ClN}_3^+\cdot\text{Cl}^-$, the cation is effectively planar and is protonated at the N atom adjacent to the amino group. Four different N—H...Cl hydrogen bonds serve to connect the constituent ions into supramolecular double chains running parallel to the b axis.

Related literature

For synthesis, see: Steck *et al.* (1954). For general background, see: Allen (2002); Ishida *et al.* (1994); Pitarch *et al.* (1974); Herter *et al.* (1989); Guery *et al.* (2001). For related structures, see: Gong & Krische (2005); Gao (2007).



Experimental

Crystal data

$\text{C}_4\text{H}_5\text{ClN}_3^+\cdot\text{Cl}^-$	$\gamma = 84.015$ (8)°
$M_r = 166.01$	$V = 342.09$ (5) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.1543$ (5) Å	Mo $K\alpha$ radiation
$b = 6.4278$ (5) Å	$\mu = 0.86$ mm ⁻¹
$c = 9.0298$ (9) Å	$T = 123$ (2) K
$\alpha = 81.763$ (4)°	$0.35 \times 0.25 \times 0.20$ mm
$\beta = 75.980$ (5)°	

Data collection

Bruker SMART CCD area-detector diffractometer	3627 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	1225 independent reflections
$T_{\min} = 0.770$, $T_{\max} = 0.841$	1162 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	82 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.19$	$\Delta\rho_{\text{max}} = 0.28$ e Å ⁻³
1225 reflections	$\Delta\rho_{\text{min}} = -0.48$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H4}\cdots\text{Cl2}^{\text{i}}$	0.89	2.13	3.0099 (15)	169
$\text{N1}-\text{H1A}\cdots\text{Cl2}^{\text{ii}}$	0.88	2.70	3.2642 (16)	123
$\text{N1}-\text{H1A}\cdots\text{Cl2}^{\text{i}}$	0.88	2.74	3.4585 (17)	140
$\text{N1}-\text{H1B}\cdots\text{Cl2}^{\text{iii}}$	0.88	2.32	3.1681 (17)	162

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2002); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2198).

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supplementary materials

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3-Amino-6-chloropyridazinium chloride

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Comment

Pyridazines have demonstrated versatile biological activities, for example, as anti-bacterial (Ishida *et al.*, 1994), anti-depressant (Pitarch *et al.*, 1974), and anti-hypertensive (Herter *et al.*, 1989) agents. A search of the Cambridge Structural Database (CSD, Version 5.28, May 2007; Allen, 2002) reveals that there are 639 crystal structures containing the pyridazine moiety. Pyridazines are also useful in the design of functional synthetic oligomers and polymers, and 3,6-diaminopyridazine is used in the synthesis of related monomeric, dimeric and trimeric duplex molecular strands (Gong & Krische, 2005). Finally, 3-amino-6-chloropyridazine is an important precursor in the preparation of various pyridazine intermediates (Guery *et al.*, 2001). Recently, the crystal structure of 3-amino-6-chloropyridazine was reported (Gao, 2007). Herein, the crystal structure of the title compound, [C₄H₅ClN₃]⁺Cl⁻ (I), is described.

In the cation, the chloro and amino groups are coplanar with the pyridazine ring, deviating within ± 0.0220 (8) Å. Protonation occurs at the N2 atom adjacent to the amino group. The N2—N3 distance is 1.345 (2) Å, close to the reported data for 3-amino-6-chloropyridazine, *i.e.* 1.355 (2) Å (Gao, 2007).

A series of intermolecular N—H \cdots Cl hydrogen bonds (Table 1) links molecules into a double chain that runs parallel to the *b* axis (Fig.2).

Experimental

3-Amino-6-chloropyridazine was prepared according to the literature method (Steck *et al.*, 1954). Crystals suitable for X-ray analysis were obtained by slow evaporation of an isopropanol solution held at room temperature (m.p. 490–492 K).

Refinement

H atoms were included in the riding model approximation with N—H = 0.88 or 0.89 Å and C—H = 0.95 Å, and with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{N}, \text{C})$.

Figures

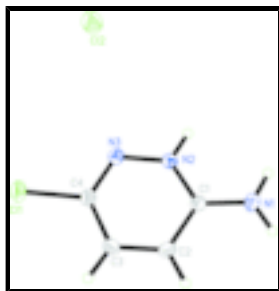


Fig. 1. Molecular structure of (I), showing 20% probability displacement ellipsoids and the atomic numbering.

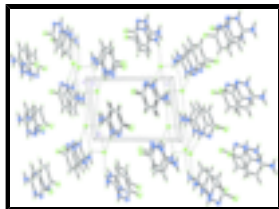


Fig. 2. The crystal packing in (I), viewed approximately down the *a* axis. Dashed lines indicate intermolecular N—H...Cl hydrogen bonds.

3-Amino-6-chloropyridazinium chloride

Crystal data

$C_4H_5ClN_3^+ \cdot Cl^-$	$Z = 2$
$M_r = 166.01$	$F_{000} = 168$
Triclinic, $P\bar{1}$	$D_x = 1.612 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 6.1543 (5) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 6.4278 (5) \text{ \AA}$	Cell parameters from 1225 reflections
$c = 9.0298 (9) \text{ \AA}$	$\theta = 2.3\text{--}25.2^\circ$
$\alpha = 81.763 (4)^\circ$	$\mu = 0.86 \text{ mm}^{-1}$
$\beta = 75.980 (5)^\circ$	$T = 123 (2) \text{ K}$
$\gamma = 84.015 (8)^\circ$	Blocks, colorless
$V = 342.09 (5) \text{ \AA}^3$	$0.35 \times 0.25 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	1225 independent reflections
Radiation source: fine-focus sealed tube	1162 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.015$
$T = 123(2) \text{ K}$	$\theta_{\text{max}} = 25.2^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.770$, $T_{\text{max}} = 0.841$	$k = -7 \rightarrow 7$
3627 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.0792P]$
$S = 1.19$	where $P = (F_o^2 + 2F_c^2)/3$
1225 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$

82 parameters

$$\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	-0.37244 (8)	0.20568 (10)	0.53712 (6)	0.0609 (2)
N3	-0.0723 (2)	0.0886 (2)	0.69127 (18)	0.0426 (4)
N2	0.0734 (2)	0.1271 (2)	0.77190 (17)	0.0410 (3)
H4	0.1547	0.0141	0.8043	0.049*
N1	0.2510 (3)	0.3270 (3)	0.89096 (18)	0.0502 (4)
H1A	0.3293	0.2126	0.9202	0.060*
H1B	0.2716	0.4495	0.9162	0.060*
C3	-0.1790 (3)	0.4590 (3)	0.6775 (2)	0.0423 (4)
H3	-0.2729	0.5729	0.6426	0.051*
C2	-0.0307 (3)	0.4902 (3)	0.7577 (2)	0.0413 (4)
H2	-0.0156	0.6276	0.7795	0.050*
C1	0.1033 (3)	0.3146 (3)	0.80952 (18)	0.0367 (4)
C4	-0.1916 (3)	0.2518 (3)	0.64622 (19)	0.0408 (4)
Cl2	0.62082 (8)	0.21076 (7)	0.10075 (5)	0.0490 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0485 (3)	0.0797 (4)	0.0665 (4)	-0.0034 (3)	-0.0288 (2)	-0.0225 (3)
N3	0.0379 (7)	0.0423 (8)	0.0525 (8)	-0.0043 (6)	-0.0144 (6)	-0.0145 (7)
N2	0.0412 (7)	0.0329 (7)	0.0528 (8)	0.0016 (6)	-0.0182 (6)	-0.0085 (6)
N1	0.0533 (9)	0.0475 (9)	0.0591 (10)	-0.0018 (7)	-0.0276 (8)	-0.0139 (7)
C3	0.0426 (9)	0.0421 (10)	0.0417 (9)	0.0055 (7)	-0.0120 (7)	-0.0052 (7)
C2	0.0495 (9)	0.0336 (9)	0.0416 (8)	-0.0009 (7)	-0.0099 (7)	-0.0100 (7)
C1	0.0362 (8)	0.0376 (9)	0.0376 (8)	-0.0028 (7)	-0.0089 (6)	-0.0079 (7)
C4	0.0340 (8)	0.0503 (10)	0.0407 (8)	-0.0035 (7)	-0.0099 (7)	-0.0119 (7)
Cl2	0.0535 (3)	0.0369 (3)	0.0631 (3)	0.0026 (2)	-0.0287 (2)	-0.0058 (2)

supplementary materials

Geometric parameters (\AA , $^\circ$)

C1—C4	1.7265 (17)	N1—H1B	0.8800
N3—C4	1.292 (2)	C3—C2	1.341 (3)
N3—N2	1.345 (2)	C3—C4	1.414 (3)
N2—C1	1.340 (2)	C3—H3	0.9500
N2—H4	0.8930	C2—C1	1.419 (2)
N1—C1	1.315 (2)	C2—H2	0.9500
N1—H1A	0.8801		
C4—N3—N2	115.16 (15)	C3—C2—C1	118.89 (16)
C1—N2—N3	126.48 (15)	C3—C2—H2	120.6
C1—N2—H4	118.2	C1—C2—H2	120.6
N3—N2—H4	115.3	N1—C1—N2	119.45 (16)
C1—N1—H1A	120.0	N1—C1—C2	123.89 (16)
C1—N1—H1B	120.0	N2—C1—C2	116.66 (15)
H1A—N1—H1B	120.0	N3—C4—C3	124.68 (16)
C2—C3—C4	118.11 (16)	N3—C4—C11	115.56 (13)
C2—C3—H3	120.9	C3—C4—C11	119.74 (14)
C4—C3—H3	120.9		
C4—N3—N2—C1	0.6 (3)	C3—C2—C1—N2	0.9 (2)
C4—C3—C2—C1	-1.0 (3)	N2—N3—C4—C3	-0.7 (2)
N3—N2—C1—N1	179.13 (15)	N2—N3—C4—C11	177.91 (11)
N3—N2—C1—C2	-0.7 (3)	C2—C3—C4—N3	1.0 (3)
C3—C2—C1—N1	-178.90 (16)	C2—C3—C4—C11	-177.56 (13)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H4 \cdots C12 ⁱ	0.89	2.13	3.0099 (15)	169
N1—H1A \cdots C12 ⁱⁱ	0.88	2.70	3.2642 (16)	123
N1—H1A \cdots C12 ⁱ	0.88	2.74	3.4585 (17)	140
N1—H1B \cdots C12 ⁱⁱⁱ	0.88	2.32	3.1681 (17)	162

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

Fig. 1

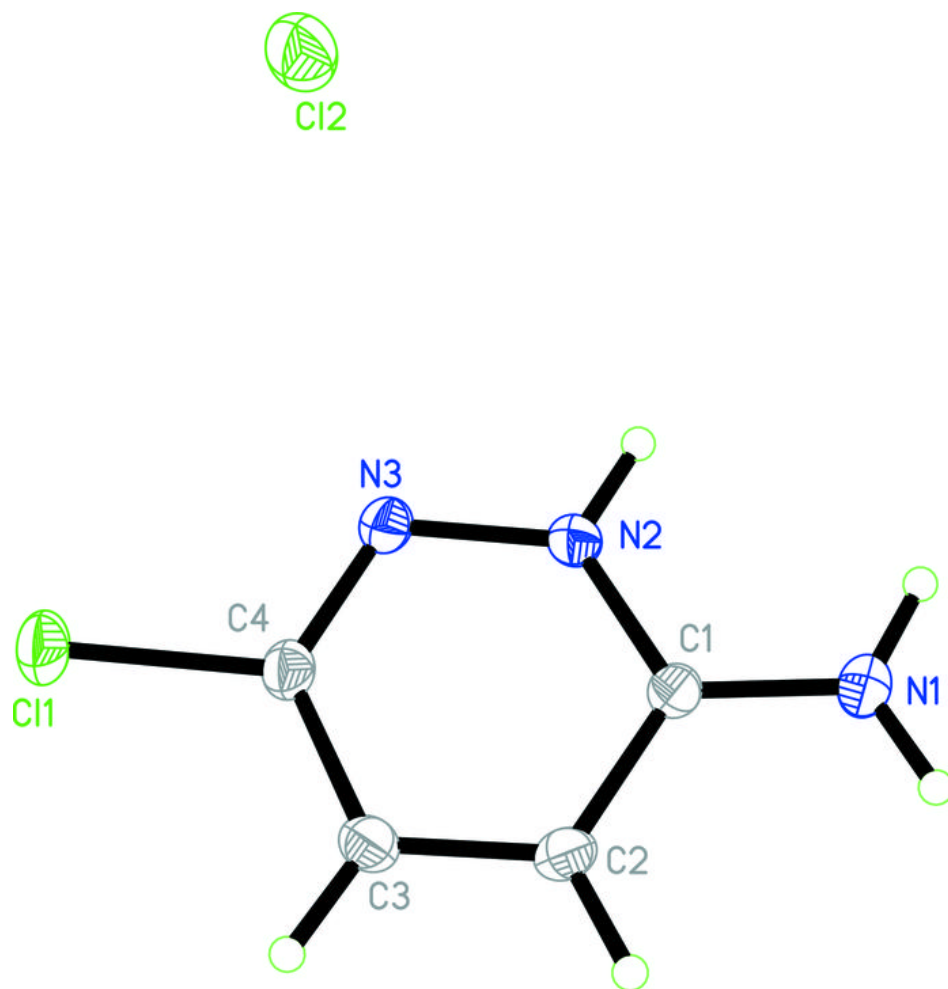


Fig. 2

