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Crystal structure of 2,6-diaminopyridinium chloride

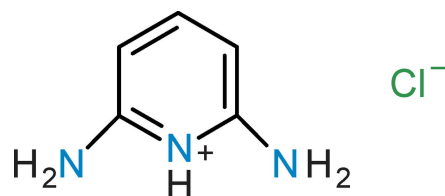
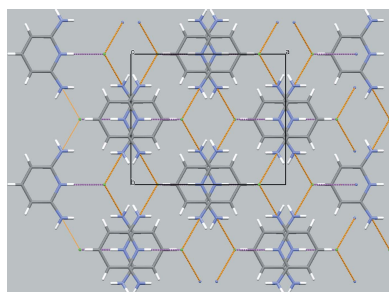
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The asymmetric unit of the title salt, $C_5H_8N_3^+ \cdot Cl^-$, comprises one half of the 2,6-diaminopyridinium cation (the other half being completed by the application of mirror symmetry) and one Cl^- counter-anion, also located on the mirror plane. The amino N atom shows a significant pyramidalization, with a dihedral angle of $30.4(14)^\circ$ between the least-squares planes of the amino group and the non-H atoms of the 2,6-diaminopyridinium moiety. In the crystal, the cationic molecules and Cl^- counter-anions are arranged in sheets parallel to (001) consisting of alternating polar and non-polar parts associated with the the Cl^- anions, pyridinium and amino moieties, and the pyridine rings, respectively. N—H...Cl interactions within the polar part, as well as slipped π – π interactions in the non-polar part, help to establish the three-dimensional network.

1. Chemical context

Pincer compounds are an important class of chelating ligands, and their metal complexes have attracted tremendous interest due to their high stability, activity, variability and applicability in organic synthesis and catalysis (Szabo & Wendt, 2014). Whereas a plethora of (mostly) precious transition-metal pincer complexes has been reported, information on group 6 pincer complexes is rather scarce. During a project aimed at the preparation and characterization of group 6 PNP pincer compounds (Öztopcu *et al.*, 2013; de Aguiar *et al.*, 2014; Mastalir *et al.*, 2016), crystals of the title salt, $C_5H_8N_3^+ \cdot Cl^-$, were obtained accidentally through hydrolysis of the employed ligand *N,N'*-bis(diisopropylphosphino)-2,6-diaminopyridine in the presence of $CrCl_3 \cdot 6H_2O$. Here we report on the crystal structure of this salt.



2. Structural commentary

The cation of the title structure is protonated at the pyridine N atom (Fig. 1). The asymmetric unit comprises half a molecule of the 2,6-diaminopyridinium cation, with a mirror plane running through the pyridinium group (N1—H1N1) and the *para*-C—H group (C3—H1C3); the Cl^- anion is also located on the mirror plane. In agreement with other 2,6-diamino-

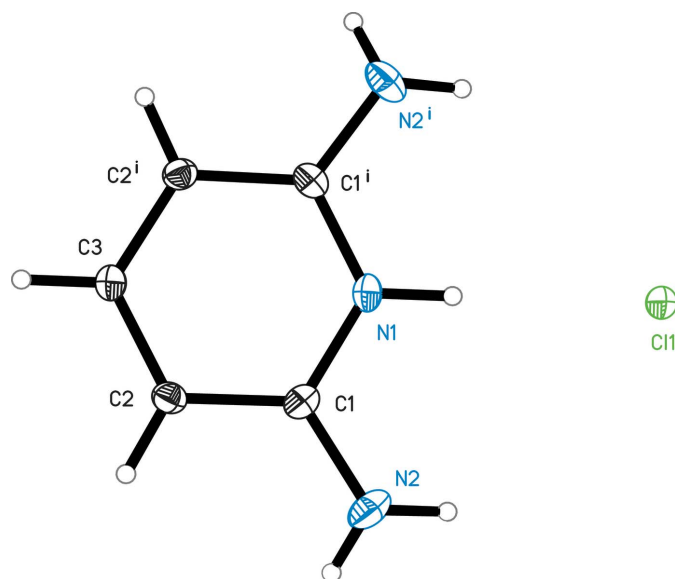


Figure 1
The molecular structure of the cation and the inorganic anion in the title structure. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x, -y, z$.]

pyridinium cations, the $C-N(H)^+-C$ angle involving the pyridinium group is enlarged [$C1-N1-C1^i = 123.37(8)^\circ$; symmetry code: (i) $x, -y, z$] whereas the angle between the pyridinium N atom and the C atom in the *ortho* position (bearing the amino group) and in the *meta* position is reduced [$N1-C1-C2 = 118.83(6)^\circ$]. This situation is reversed in 2,6-diaminopyridine due to the non-protonated ring N atom in this structure (Schwalbe *et al.*, 1987). A common feature of the non-protonated 2,6-diaminopyridine molecule and the 2,6-diaminopyridinium cation is a significant pyramidalization of the amino N atom. In the title structure, the bond angle sum at this atom (N2) deviates with 349.0° clearly from the expected

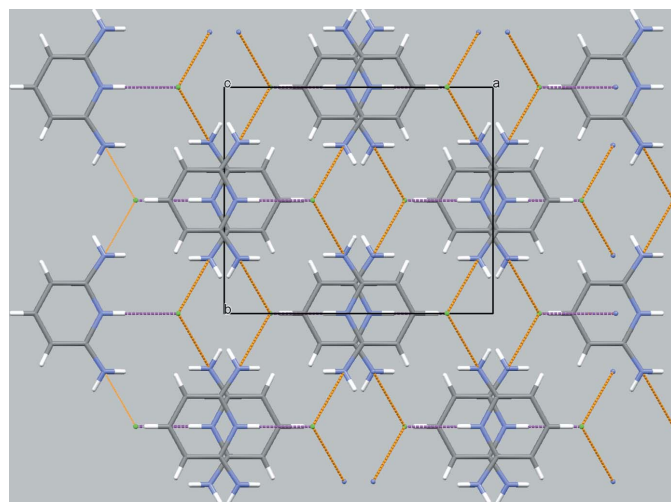


Figure 2
Crystal packing of the organic and inorganic components in the title structure in a projection along [001]. $N-H\cdots Cl$ hydrogen bonds involving the pyridinium group are shown as magenta dotted lines and those involving the amino group are shown as orange dotted lines.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N1\cdots Cl1$	0.90 (2)	2.18 (2)	3.0790 (11)	175.6 (19)
$N2-H2N2\cdots Cl1^i$	0.833 (13)	2.628 (13)	3.4086 (8)	156.5 (12)
$N2-H1N2\cdots Cl1^{ii}$	0.875 (13)	2.877 (13)	3.3601 (8)	116.8 (2)

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

360° for an ideal trigonal-planar group. The pyramidalization is also reflected by the dihedral angle of $30.4(14)^\circ$ between the least-squares planes of the amino group and the non-H atoms of the 2,6-diaminopyridinium moiety.

3. Supramolecular features

The pyridinium $N1-H1N1$ group is the donor of a nearly linear hydrogen bond to the Cl^- counter anion (Table 1). The amino group also participates in the formation of $N-H\cdots Cl$ hydrogen bonds, albeit of explicit weaker nature. One hydrogen atom ($H2N2$) is clearly involved in hydrogen bonding with an $H2N2\cdots Cl1$ distance of 2.63 \AA and an $N2-H2N2\cdots Cl1$ angle of 157° . Although the $D\cdots A$ contact involving the second hydrogen atom, $H2N2$, is 0.04 \AA shorter than that of the other hydrogen bond of this group, the comparatively long $H1N2\cdots Cl$ distance of 2.88 \AA and the very small $N2-H1N2\cdots Cl1$ angle of 117° give room for interpretation whether or not this is a real hydrogen bond.

In the crystal (Figs. 2 and 3), the cationic molecules and anions are arranged into layers with alternating polar and non-polar parts extending parallel to (001). Adjacent polar parts, comprising the Cl^- anions and the pyridinium and amino moieties, are linked through $N-H\cdots Cl$ hydrogen bonds into sheets with a thickness of $\simeq c/2$. The non-polar parts, *i.e.* the pyridine rings, interact through slipped $\pi-\pi$ stacking along [001] with a centroid-to-centroid distance of $3.5129(6) \text{ \AA}$; the corresponding plane-to-plane distance between the pyridine rings is 3.344 \AA .

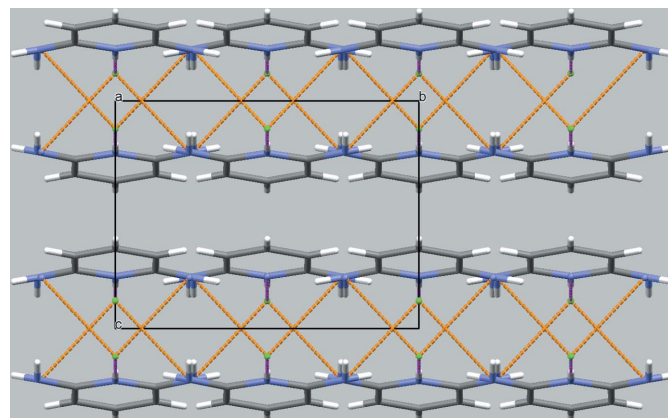


Figure 3
Crystal packing of the organic and inorganic components in the title structure in a projection along [100]. The colour code of the intermolecular interactions is as in Fig. 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₅ H ₈ N ³⁺ ·Cl ⁻
<i>M_r</i>	145.6
Crystal system, space group	Monoclinic, <i>C2/m</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.8046 (10), 9.0459 (9), 6.8108 (7)
β (°)	96.710 (2)
<i>V</i> (Å ³)	661.11 (11)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.48
Crystal size (mm)	0.52 × 0.38 × 0.23
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T_{min}</i> , <i>T_{max}</i>	0.80, 0.90
No. of measured, independent and observed [<i>I</i> > 3 σ (<i>I</i>)] reflections	9529, 1538, 1407
<i>R_{int}</i>	0.031
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.808
Refinement	
<i>R</i> [<i>F</i> ² > 3 σ (<i>F</i>)], <i>wR</i> (<i>F</i>), <i>S</i>	0.024, 0.038, 2.24
No. of reflections	1538
No. of parameters	64
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.49, -0.18

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *XP* in *SHELXL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006) and *pubCIF* (Westrip, 2010).

4. Database survey

A search in the CSD (Groom & Allen, 2014; CSD Version 5.31) revealed 87 different salts containing the 2,6-diaminopyridinium cation, with the majority of cases in the form of organic anions (46 representatives), followed by complex metal anions (31 representatives). Two structures are reported that contain additional metal cations and inorganic anions, and eight representatives are compiled with inorganic anions only, including the SiF₆²⁻ salt (CSD code FOSXER; Gelmboldt *et al.*, 2009), the Br⁻ salt (GOLMIF; Turrell *et al.*, 2010), the BF₄⁻ salt (IFOQAW; Benito-Garagorri *et al.*; 2007), the Br⁻ salt monohydrate (ILINEW; Haddad & Al-Far, 2003), the hydrogensulfate sulfate salt (KORRAM; Said & Naili, 2014), the ClO₄⁻ salt (MIGWOP; Jazdoń *et al.*, 2007), the H₂PO₄⁻ salt (QEDHUE; Yu, 2012) and the NO₃⁻ salt (XAKVAG; Kristiansson, 2000). It should be noted that the chemically most related anhydrous Br⁻ salt crystallizes in space group *I42d* and hence shows no isotypism with the title Cl⁻ salt.

5. Synthesis and crystallization

N,N'-bis(diisopropylphosphino)-2,6-diaminopyridine (0.2 g, 0.53 mmol) was dissolved in dry tetrahydrofuran (5 ml) under argon atmosphere. CrCl₃·6H₂O (0.134 g, 0.51 mmol) was added and the resulting mixture stirred for 4 h at room

temperature. The formed purple solid was filtered off, washed with dry diethyl ether and dried. The solid was redissolved in acetonitrile for crystallization initiated by solvent diffusion with diethyl ether. The title compound grew in the form of yellow crystals as the only solid product. We assume that the Lewis acid CrCl₃ in combination with water is able to cleave the P–N bond of the pincer compound accompanied by an *in situ* formation of HCl which eventually yields the title compound.

6. Refinement

All H atoms were clearly discernible from difference Fourier maps and were refined freely. Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Crystal structure of 2,6-diaminopyridinium chloride

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2,6-Diaminopyridin-1-ium chloride

Crystal data

$C_5H_8N^{3+} \cdot Cl^-$

$M_r = 145.6$

Monoclinic, *C2/m*

Hall symbol: $-C\ 2y$

$a = 10.8046$ (10) Å

$b = 9.0459$ (9) Å

$c = 6.8108$ (7) Å

$\beta = 96.710$ (2)°

$V = 661.11$ (11) Å³

$Z = 4$

$F(000) = 304$

$D_x = 1.462$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6316 reflections

$\theta = 2.9\text{--}35.5^\circ$

$\mu = 0.48$ mm⁻¹

$T = 100$ K

Block, yellow

$0.52 \times 0.38 \times 0.23$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: X-ray tube

Graphite monochromator

ω - and φ -scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2014)

$T_{\min} = 0.80$, $T_{\max} = 0.90$

9529 measured reflections

1538 independent reflections

1407 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 35.0^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -17 \rightarrow 17$

$k = -14 \rightarrow 14$

$l = -10 \rightarrow 10$

Refinement

Refinement on F

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.038$

$S = 2.24$

1538 reflections

64 parameters

0 restraints

0 constraints

All H-atom parameters refined

Weighting scheme based on measured s.u.'s $w =$

$1/(\sigma^2(F) + 0.0001F^2)$

$(\Delta/\sigma)_{\max} = 0.030$

$\Delta\rho_{\max} = 0.49$ e Å⁻³

$\Delta\rho_{\min} = -0.18$ e Å⁻³

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.17115 (2)	0	0.12206 (3)	0.01401 (7)
N1	0.45600 (9)	0	0.22925 (12)	0.0132 (2)
N2	0.44617 (7)	0.25682 (8)	0.22357 (10)	0.01951 (18)
C1	0.51532 (7)	0.13257 (7)	0.25660 (9)	0.01272 (16)
C2	0.64225 (7)	0.13396 (7)	0.32011 (10)	0.01334 (17)
C3	0.70393 (10)	0	0.35111 (14)	0.0136 (2)
H1C2	0.6796 (9)	0.2256 (14)	0.3421 (16)	0.019 (3)*
H1C3	0.7905 (16)	0	0.392 (2)	0.015 (3)*
H1N2	0.3742 (16)	0.2574 (17)	0.150 (2)	0.046 (4)*
H2N2	0.4841 (12)	0.3350 (15)	0.2058 (19)	0.032 (3)*
H1N1	0.3735 (19)	0	0.191 (3)	0.039 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.01121 (13)	0.01270 (11)	0.01763 (12)	0	-0.00037 (8)	0
N1	0.0093 (4)	0.0176 (4)	0.0128 (3)	0	0.0018 (3)	0
N2	0.0192 (3)	0.0187 (3)	0.0214 (3)	0.0075 (2)	0.0056 (2)	0.0065 (2)
C1	0.0137 (3)	0.0143 (3)	0.0107 (2)	0.0025 (2)	0.0039 (2)	0.00180 (19)
C2	0.0136 (3)	0.0118 (3)	0.0149 (3)	-0.0012 (2)	0.0026 (2)	-0.00027 (19)
C3	0.0108 (4)	0.0154 (4)	0.0145 (4)	0	0.0011 (3)	0

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

N1—C1	1.3622 (8)	C1—C2	1.3890 (10)
N1—C1	1.3622 (8)	C2—C3	1.3872 (9)
N1—H1N1	0.90 (2)	C2—H1C2	0.927 (12)
N2—C1	1.3538 (10)	C3—H1C3	0.944 (17)
N2—H1N2	0.875 (16)	C3—C2	1.3872 (9)
N2—H2N2	0.833 (13)		
C1—N1—C1	123.37 (8)	N2—C1—C2	123.35 (6)
C1—N1—H1N1	118.32 (4)	C1—C2—C3	118.60 (7)
C1—N1—H1N1	118.32 (4)	C1—C2—H1C2	117.0 (6)
C1—N2—H1N2	122.5 (10)	C3—C2—H1C2	124.4 (6)
C1—N2—H2N2	117.2 (9)	C2—C3—C2	121.75 (9)
H1N2—N2—H2N2	109.3 (13)	C2—C3—H1C3	119.12 (5)
N1—C1—N2	117.81 (7)	C2—C3—H1C3	119.12 (5)
N1—C1—C2	118.83 (6)		

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N1 \cdots C11	0.90 (2)	2.18 (2)	3.0790 (11)	175.6 (19)

N2—H2N2...C11 ⁱ	0.833 (13)	2.628 (13)	3.4086 (8)	156.5 (12)
N2—H1N2...C11 ⁱⁱ	0.875 (13)	2.877 (13)	3.3601 (8)	116.8 (2)

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