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2,6-Diaminopyridinium perchlorate

Monika Jazdoń, Wanda Radecka-Paryzek and Maciej Kubicki*

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Correspondence e-mail: mkubicki@amu.edu.pl

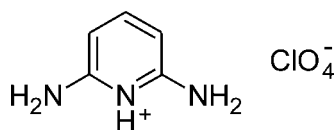
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.044; wR factor = 0.097; data-to-parameter ratio = 11.0.

In the title salt, $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{ClO}_4^-$, a mirror plane runs through the ring N atom and the *para*-C atom of the cation, and also through Cl and one O atom of the anion. The anion is disordered equally over two positions. A network of N—H \cdots O hydrogen bonds connects the cations and anions into layers, forming a stair-like structure.

Related literature

There are a number of structures of 2,6-diaminopyridinium salts with different anions. For example, see Bertolasi *et al.* (2001). For related literature, see Cao *et al.* (2006), Liu *et al.* (2001), Scriven *et al.* (1996).



Experimental

Crystal data

 $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{ClO}_4^-$ $M_r = 209.59$ Monoclinic, $P2_1/m$ $a = 5.0007$ (8) Å $b = 10.3776$ (17) Å $c = 8.2345$ (14) Å $\beta = 100.535$ (17)° $V = 420.13$ (12) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.44$ mm⁻¹ $T = 294$ (1) K $0.25 \times 0.15 \times 0.1$ mm

Data collection

Kuma KM-4-CCD four-circle diffractometer

Absorption correction: none

2095 measured reflections

868 independent reflections

638 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$ $wR(F^2) = 0.097$ $S = 1.06$

868 reflections

79 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2 ⁱ	0.86	2.19	2.988 (9)	154
N2—H2A \cdots O2 ⁱ	0.86	2.26	3.034 (10)	149
N2—H2B \cdots O1 ⁱⁱ	0.86	2.45	3.025 (2)	124
C4—H4 \cdots O3 ⁱⁱⁱ	0.93	2.56	3.474 (5)	169

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2115).

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supplementary materials

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2,6-Diaminopyridinium perchlorate

M. Jazdon, W. Radecka-Paryzek and M. Kubicki

Comment

The 2,6-diaminopyridine is used as component for the self-assembled supramolecular architectures displaying interesting structures (Liu *et al.*, 2001) useful as a pharmaceutical intermediate for the synthesis of analgesic drugs (Scriven *et al.*, 1996) and in the construction of electrochemical sensor for detection of ascorbic acid (Cao *et al.*, 2006). The title compound was isolated in the course of our studies of Schiff base metal complexes with novel physico-chemical properties and potential applications.

The compound I (Fig. 1) crystallizes in the monoclinic space group $P2_1/m$ with two molecules in the unit cell with asymmetric unit comprising half of a molecule. The crystallographic mirror plane passes the pyridinium ring along N1...C4 line (H1, N1 and C4 all lie in the plane) while in the anion Cl and one of oxygen atoms are in this plane. The anion is moreover disordered over two positions with occupancy factors 0.5 for involving atoms. The attempts to refine the structure in non-centrosymmetric $P2_1$ space group gave results inferior to the centrosymmetric model. The cations and anions are connected by means of N—H...O hydrogen bonds into layers (Tale 1, Fig. 2). These layers are also connected by N—H...O hydrogen bonds into the stair-like structure (Fig. 3).

Experimental

To a solution of lanthanum(III) perchlorate (0.1 mmol) in acetonitrile (10 ml), 2,6-diaminopyridine (0.2 mmol) in acetonitrile (10 ml) was added with stirring. The reaction was carried out for 24 h at room temperature. The solution volume was then reduced to 10 ml by roto-evaporation and very small amount of precipitate was formed on addition of diethyl ether. The solution over the precipitate was separated and left to evaporate at room temperature affording transparent long needles of I after three days.

Refinement

Hydrogen atoms were put in idealized positions and refined as 'riding model' with U_{iso} set at 1.2 times U_{eq} of appropriate carrier atoms. The disordered atoms of the anion were found in difference Fourier map and anisotropically refined without restraints.

Figures

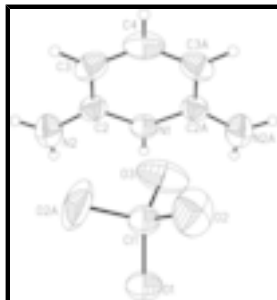


Fig. 1. Molecular structure of I with displacement parameters scaled at the 50% probability level (Siemens, 1989) and numbering scheme. The hydrogen atoms are drawn as spheres with arbitrary radii. Only one orientation of disordered perchlorate anion is shown.

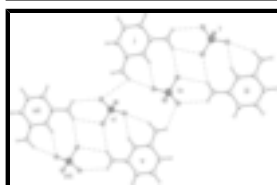


Fig. 2. The layer of the cations and anions connected by hydrogen bonds (Siemens, 1989). Hydrogen bonds are drawn as dashed lines. The symmetry codes used: (i) x, y, z ; (ii) $x, y, -1 + z$; (iii) $2 - x, -y, -z$; (iv) $2 - x, -y, 1 - z$; (v) $2 - x, 1/2 + y, -z$; (vi) $2 - x, 1/2 + y, 1 - z$; (vii) $x, 1 + y, z$; (viii) $x, 1 + y, -1 + z$.

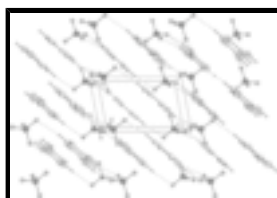
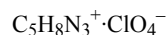


Fig. 3. The crystal packing along a direction (Siemens, 1989). Hydrogen bonds are shown as dashed lines.

2,6-Diaminopyridinium perchlorate

Crystal data



$M_r = 209.59$

Monoclinic, $P2_1/m$

Hall symbol: $-P\ 2yb$

$a = 5.0007\ (8)\ \text{\AA}$

$b = 10.3776\ (17)\ \text{\AA}$

$c = 8.2345\ (14)\ \text{\AA}$

$\beta = 100.535\ (17)^\circ$

$V = 420.13\ (12)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 216$

$D_x = 1.657\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2311 reflections

$\theta = 4\text{--}24^\circ$

$\mu = 0.44\ \text{mm}^{-1}$

$T = 294\ (1)\ \text{K}$

Block, colourless

$0.25 \times 0.15 \times 0.1\ \text{mm}$

Data collection

Kuma KM-4-CCD four-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294\ (1)\ \text{K}$

ω scan

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

$R_{\text{int}} = 0.028$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 3.2^\circ$

$h = -6 \rightarrow 5$

Absorption correction: none
 2095 measured reflections
 868 independent reflections

$k = -12 \rightarrow 12$
 $l = -8 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.097$	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.0483P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
868 reflections	$(\Delta/\sigma)_{\max} < 0.001$
79 parameters	$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$
	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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.5846 (5)	0.2500	0.2196 (3)	0.0384 (7)	
H1	0.7017	0.2500	0.1550	0.046*	
C2	0.4989 (5)	0.1342 (2)	0.2668 (3)	0.0410 (6)	
N2	0.6064 (4)	0.0285 (2)	0.2109 (3)	0.0649 (7)	
H2A	0.7248	0.0358	0.1477	0.078*	
H2B	0.5571	-0.0466	0.2382	0.078*	
C3	0.3110 (5)	0.1340 (3)	0.3701 (3)	0.0518 (7)	
H3	0.2458	0.0569	0.4052	0.062*	
C4	0.2224 (7)	0.2500	0.4198 (4)	0.0546 (11)	
H4	0.0969	0.2500	0.4903	0.066*	
Cl1	0.97841 (16)	0.2500	0.86291 (10)	0.0388 (3)	
O1	1.2550 (4)	0.2500	0.8438 (3)	0.0529 (7)	
O2	0.936 (2)	0.3390 (8)	0.9844 (9)	0.070 (2)	0.50
O3	0.8079 (6)	0.2124 (6)	0.7121 (4)	0.073 (3)	0.50
O2A	0.912 (2)	0.3748 (8)	0.9156 (12)	0.092 (3)	0.50

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0342 (15)	0.0461 (19)	0.0374 (16)	0.000	0.0135 (12)	0.000
C2	0.0370 (13)	0.0428 (16)	0.0416 (15)	-0.0033 (11)	0.0027 (11)	0.0009 (12)
N2	0.0677 (16)	0.0434 (15)	0.0858 (18)	0.0017 (12)	0.0201 (13)	-0.0080 (13)
C3	0.0452 (15)	0.064 (2)	0.0456 (16)	-0.0120 (13)	0.0057 (12)	0.0111 (13)
C4	0.040 (2)	0.089 (3)	0.037 (2)	0.000	0.0139 (16)	0.000
C11	0.0344 (5)	0.0420 (6)	0.0421 (5)	0.000	0.0128 (3)	0.000
O1	0.0330 (13)	0.0560 (17)	0.0736 (18)	0.000	0.0205 (11)	0.000
O2	0.087 (4)	0.065 (5)	0.066 (4)	-0.001 (4)	0.031 (3)	-0.026 (3)
O3	0.0501 (18)	0.124 (8)	0.0438 (19)	-0.023 (3)	0.0027 (14)	-0.003 (2)
O2A	0.095 (5)	0.038 (4)	0.161 (10)	0.026 (3)	0.071 (6)	0.002 (4)

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

N1—C2 ⁱ	1.356 (3)	C4—C3 ⁱ	1.371 (3)
N1—C2	1.356 (3)	C4—H4	0.9300
N1—H1	0.8600	C11—O2	1.406 (9)
C2—N2	1.339 (3)	C11—O2 ⁱ	1.406 (9)
C2—C3	1.378 (4)	C11—O1	1.421 (2)
N2—H2A	0.8600	C11—O2A	1.424 (9)
N2—H2B	0.8600	C11—O2A ⁱ	1.424 (9)
C3—C4	1.371 (3)	C11—O3 ⁱ	1.426 (4)
C3—H3	0.9300	C11—O3	1.426 (4)
C2 ⁱ —N1—C2	124.7 (3)	C3—C4—H4	118.6
C2 ⁱ —N1—H1	117.6	O2—C11—O1	110.9 (4)
C2—N1—H1	117.6	O2 ⁱ —C11—O1	110.9 (4)
N2—C2—N1	117.3 (2)	O2 ⁱ —C11—O2A	107.8 (4)
N2—C2—C3	124.9 (3)	O1—C11—O2A	108.6 (4)
N1—C2—C3	117.7 (2)	O2—C11—O2A ⁱ	107.8 (4)
C2—N2—H2A	120.0	O1—C11—O2A ⁱ	108.6 (4)
C2—N2—H2B	120.0	O2—C11—O3 ⁱ	107.2 (4)
H2A—N2—H2B	120.0	O1—C11—O3 ⁱ	110.04 (19)
C4—C3—C2	118.5 (3)	O2A ⁱ —C11—O3 ⁱ	112.2 (5)
C4—C3—H3	120.8	O2 ⁱ —C11—O3	107.2 (4)
C2—C3—H3	120.8	O1—C11—O3	110.04 (18)
C3 ⁱ —C4—C3	122.8 (4)	O2A—C11—O3	112.2 (5)
C3 ⁱ —C4—H4	118.6		
C2 ⁱ —N1—C2—N2	-179.11 (18)	N1—C2—C3—C4	-0.3 (4)
C2 ⁱ —N1—C2—C3	0.1 (4)	C2—C3—C4—C3 ⁱ	0.6 (5)
N2—C2—C3—C4	178.8 (3)		

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2 ⁱⁱ	0.86	2.19	2.988 (9)	154
N2—H2A \cdots O2 ⁱⁱ	0.86	2.26	3.034 (10)	149
N2—H2B \cdots O1 ⁱⁱⁱ	0.86	2.45	3.025 (2)	124
C4—H4 \cdots O3 ^{iv}	0.93	2.56	3.474 (5)	169

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

Fig. 1

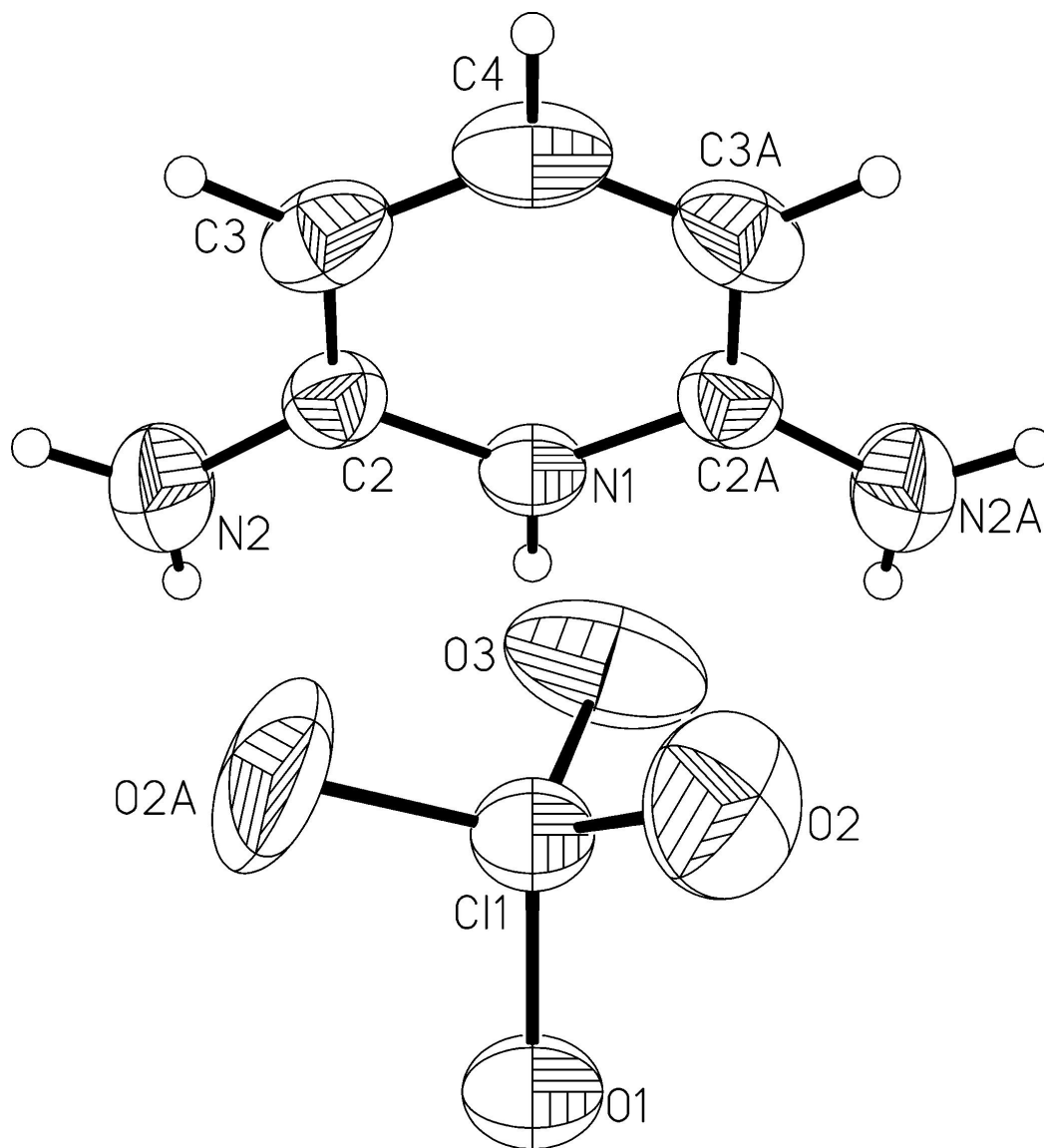


Fig. 2

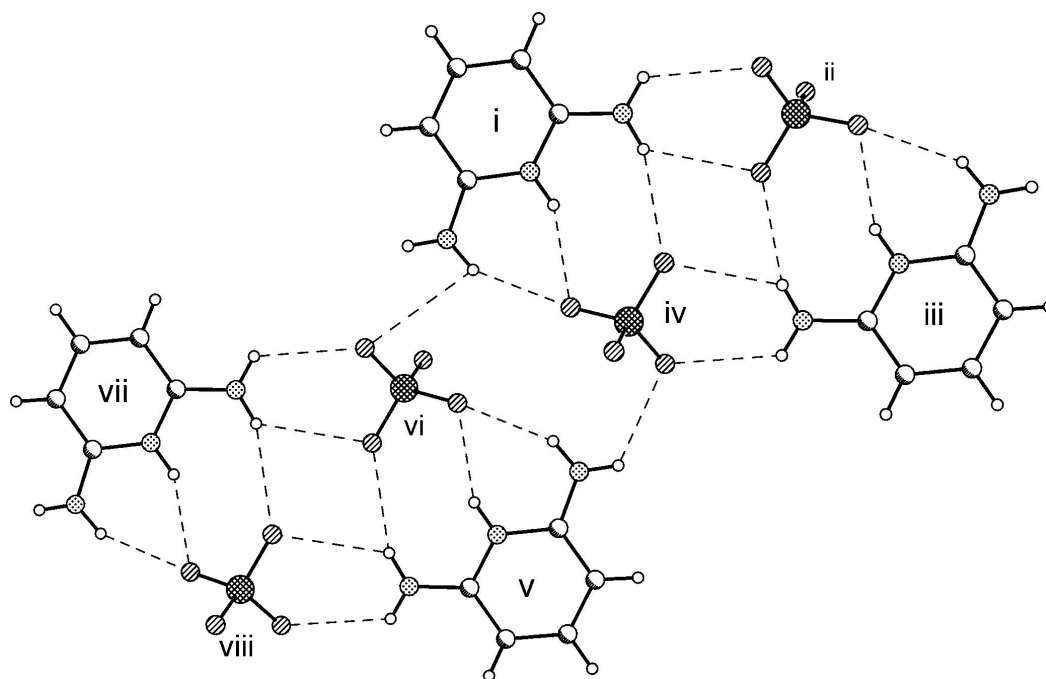


Fig. 3

