

2,2'-(*p*-Phenylenediimino)dipyridinium  
dichloride hexahydrateMaria Gdaniec,<sup>a</sup> Igor  
Bensemam<sup>b</sup> and  
Tadeusz Połowski<sup>b\*</sup><sup>a</sup>Faculty of Chemistry, Adam Mickiewicz  
University, 60-780 Poznań, Poland, and  
<sup>b</sup>Department of Chemistry, Technical University  
of Gdańsk, 80-952 Gdańsk, Poland

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

Received 5 June 2006  
Accepted 10 July 2006

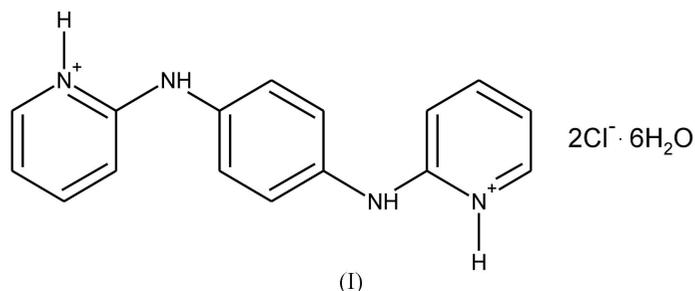
In the crystal structure of the title compound,  $C_{16}H_{16}N_4^{2+} \cdot 2Cl^- \cdot 6H_2O$ , the 2,2'-(*p*-phenylenediimino)-dipyridinium cation has inversion symmetry. The chloride ions and water molecules are linked *via*  $O-H \cdots O$  and  $O-H \cdots Cl^-$  hydrogen bonds into an infinite two-dimensional network parallel to the (001) plane. The cations, as fourfold hydrogen-bond donors, connect neighbouring  $[Cl^- \cdot (H_2O)_3]_{\infty}$  anionic networks into polymeric three-dimensional hydrogen-bonded assemblies.

## Key indicators

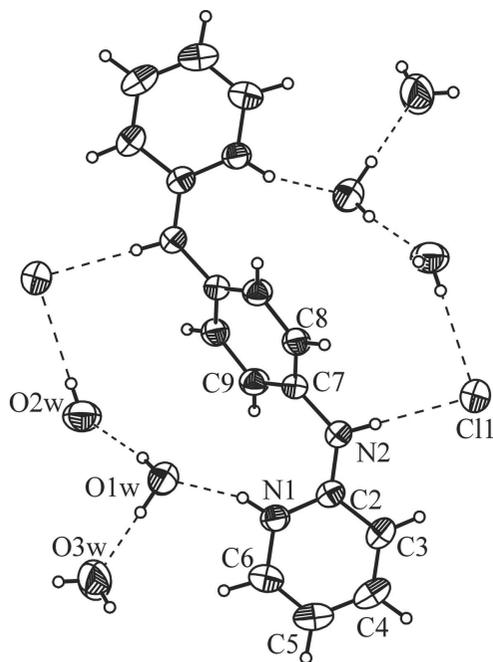
Single-crystal X-ray study  
 $T = 170$  K  
Mean  $\sigma(C-C) = 0.003$  Å  
 $R$  factor = 0.036  
 $wR$  factor = 0.101  
Data-to-parameter ratio = 13.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## Comment

*N,N'*-Bis(2-pyridyl)aryldiamines with two proton-donor and two proton-acceptor sites have been used as versatile substrates in the synthesis of extended supramolecular arrays (Bensemam *et al.*, 2002, 2003; Gdaniec *et al.*, 2002, 2005). Whereas *N,N'*-bis(2-pyridyl)aryldiamines cocrystallize relatively easily with dicarboxylic acids, forming good-quality crystals consisting of predictable one-dimensional hydrogen-bond assemblies (Bensemam *et al.*, 2003), their salts with simple inorganic acids, with only a few exceptions, are difficult to crystallize. Here, we report the crystal structure of 2,2'-(*p*-phenylenediimino)dipyridinium dichloride hexahydrate, (I), which was obtained as an intermediate product in the synthesis of *N,N'*-di-2-pyridylbenzene-1,4-diamine (PDAB).



The asymmetric unit of (I) consists of one half of the centrosymmetric PDAB dication, one chloride ion and three water molecules (Fig. 1). In the crystalline state, PDAB has been observed in a variety of conformations, ranging from a nearly planar *Z,Z* form in its cocrystal with phenazine (Gdaniec *et al.*, 2005) to strongly twisted *Z,Z* and *E,E* forms in its polymorphs (Bensemam *et al.*, 2002). It was obvious that, for steric reasons, double protonation of the PDAB occurring at the pyridine N atoms should force the dication to adopt a non-planar conformation. In (I), the pyridinium and benzene units are inclined at an angle of  $51.85(9)^\circ$ . They are rotated with respect to the  $C2/N2/C7$  plane; however, as in the free base, the twist about the  $N2-C_{ar}$  bond is significantly smaller



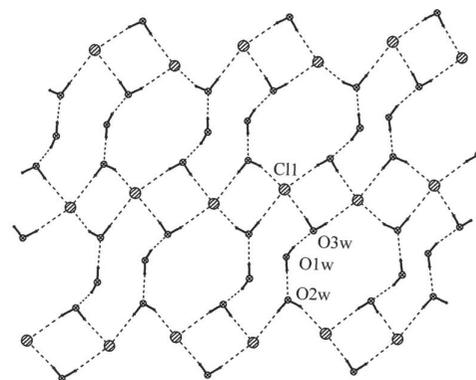
**Figure 1**  
The structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Labelled atoms are related to unlabelled atoms by the symmetry operation  $(1 - x, 2 - y, -z)$ .

for the pyridinium ring than for the aryl unit (Table 1). The *N*-aryl-2-pyridiniumamine group adopts a twisted *Z* conformation which prevents cation from binding the halide ions in a chelating mode.

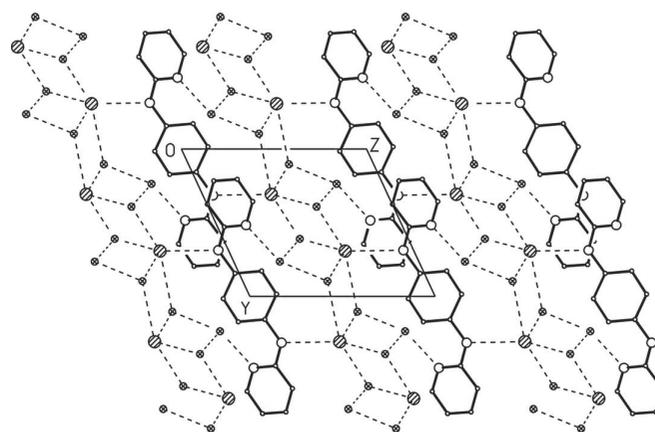
The geometrical parameters of hydrogen bonds listed in Table 2 are in agreement with the values reported by Steiner (1998). The dications, which act as fourfold donors in hydrogen bonding, take part in  $N-H \cdots O$  and  $N-H^+ \cdots Cl^-$  interactions. The chloride ions and water molecules are linked via  $O-H \cdots O$  and  $O-H \cdots Cl^-$  hydrogen bonds into an infinite two-dimensional anionic network parallel to the (001) plane (Fig. 2*a* and Table 2). The cations connect the neighbouring anionic  $[Cl^-(H_2O)_3]_\infty$  networks, generating a polymeric three-dimensional hydrogen-bonded assembly (Fig. 2*b*). Each water molecule simultaneously acts as a double donor and single acceptor in hydrogen bonding, whereas the chloride ion acts as a fivefold acceptor. The proton donors form a distorted square-pyramidal arrangement around the  $Cl^-$  ion, with  $O2W(x, y, -1 + z)$  situated in the apical position; the basal plane of the square pyramidal environment is open for electrostatic interaction with the electron-deficient pyridinium ring. The  $Cl^-$  ion is located 3.4851 (11) Å from the mean plane of the pyridinium ring at the symmetry position  $(1 - x, 1 - y, -z)$  and 3.54 Å from its centroid.

## Experimental

The title compound, (I), was prepared as an intermediate product in the synthesis of *N,N'*-di-2-pyridylbenzene-1,4-diamine (Bensemann *et al.*, 2002). The single crystal used for the X-ray analysis was obtained by recrystallization from water.



(a)



(b)

**Figure 2**

Hydrogen-bond interactions (dashed lines) in (I), showing (a) the two-dimensional network formed by  $Cl^-$  anions and water molecules and (b) the crystal packing viewed along the *a* axis, with H atoms omitted for clarity.

### Crystal data

$C_{16}H_{16}N_4^{2+} \cdot 2Cl^- \cdot 6H_2O$   
 $M_r = 443.32$   
 Triclinic,  $P\bar{1}$   
 $a = 8.2870$  (10) Å  
 $b = 8.3104$  (10) Å  
 $c = 9.1906$  (12) Å  
 $\alpha = 65.572$  (12)°  
 $\beta = 89.030$  (10)°  
 $\gamma = 75.472$  (10)°

$V = 555.14$  (14) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.326$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.33$  mm<sup>-1</sup>  
 $T = 170$  (2) K  
 Block, colourless  
 0.40 × 0.40 × 0.40 mm

### Data collection

Kuma KM4CCD  $\kappa$ -geometry diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 3011 measured reflections

1942 independent reflections  
 1757 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.027$   
 $\theta_{max} = 25.0^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.101$   
 $S = 1.07$   
 1942 reflections  
 142 parameters  
 Only H-atom displacement parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.1307P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.22$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.064 (10)

**Table 1**

Selected geometric parameters (Å, °).

N1—C2	1.343 (2)	N2—C2	1.338 (2)
N1—C6	1.362 (2)	N2—C7	1.4264 (19)
C2—N1—C6	122.08 (15)	C2—N2—C7	128.24 (13)
C7—N2—C2—N1	−13.8 (3)	C2—N2—C7—C9	−45.1 (2)

**Table 2**

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>
O1W—H1WA···O2W	0.85	1.94	2.779 (2)	168
O1W—H1WB···O3W	0.85	1.91	2.759 (2)	175
O2W—H2WA···C1 <sup>i</sup>	0.85	2.35	3.1957 (17)	175
O2W—H2WB···C1 <sup>ii</sup>	0.85	2.37	3.2067 (16)	168
O3W—H3WA···C1 <sup>iii</sup>	0.85	2.36	3.1986 (17)	169
O3W—H3WB···C1 <sup>iv</sup>	0.85	2.39	3.2036 (17)	161
N1—H1···O1W	0.90	1.85	2.7121 (18)	160
N2—H2···C1	0.90	2.31	3.2056 (15)	179

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

All H atoms were located in electron-density difference maps. H atom distances were standardized to 0.85, 0.90 and 0.96 Å for O—H,

N—H and C—H bonds, respectively. H atoms were refined as riding on their parent atoms with freely refined  $U_{\text{iso}}$  values.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2000); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

Financial support from the Committee of Scientific Research (project No. 3 T09 098 18) is gratefully acknowledged.

## References

- Bensemam, I., Gdaniec, M., Łakomecka, K., Milewska, M. J. & Połoński, T. (2003). *Org. Biomol. Chem.* **1**, 1425–1434.
- Bensemam, I., Gdaniec, M. & Połoński, T. (2002). *New J. Chem.* **26**, 448–456.
- Gdaniec, M., Bensemam, I. & Połoński, T. (2002). *Acta Cryst.* **C58**, o735–o738.
- Gdaniec, M., Bensemam, I. & Połoński, T. (2005). *CrystEngComm*, **7**, 433–438.
- Oxford Diffraction (2000). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.163. Oxford Diffraction, Abingdon, Oxfordshire, England.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Steiner, T. (1998). *Acta Cryst.* **B54**, 456–463.