

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 1,1'-Methylenedipyridinium dichloride monohydrate

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Received 20 April 2010; accepted 24 April 2010

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.022;  $wR$  factor = 0.056; data-to-parameter ratio = 17.8.

In the crystal structure of the title salt,  $\text{C}_{11}\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{H}_2\text{O}$ , the dication adopts a butterfly shape [dihedral angle between rings =  $69.0(1)^\circ$ ] with the water molecule lying in the V-shaped cavity. Each O—H bond of the water molecule lies parallel to an aromatic ring and forms an O—H $\cdots$ Cl interaction to a chloride anion. The methylene C atom in the dication and the water O atoms lie on special positions of twofold site symmetry.

## Related literature

For the synthesis, see: Almarzoqi *et al.* (1986). For the crystal structure of dipyridiniummethane diiodide, see: Brüdgam & Hartl (1986). For background to the use of similar compounds in the synthesis of coordination polymers, see: Niu *et al.* (2008).



## Experimental

## Crystal data

 $\text{C}_{11}\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{H}_2\text{O}$   
 $M_r = 261.14$ 

 Orthorhombic, *Fdd2*  
 $a = 16.3384(15)$  Å

 $b = 19.0958(18)$  Å  
 $c = 7.7916(7)$  Å  
 $V = 2430.9(4)$  Å<sup>3</sup>  
 $Z = 8$ 

 Mo  $K\alpha$  radiation  
 $\mu = 0.51$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.30 \times 0.15 \times 0.10$  mm

## Data collection

 Bruker SMART APEX  
 diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.861$ ,  $T_{\max} = 0.950$ 

 5641 measured reflections  
 1389 independent reflections  
 1333 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.056$   
 $S = 1.04$   
 1389 reflections  
 78 parameters  
 2 restraints

 H atoms treated by a mixture of  
 independent and constrained  
 refinement  
 $\Delta\rho_{\max} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.16$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 642 Friedel pairs  
 Flack parameter: 0.01 (6)

Table 1

Hydrogen-bond geometry (Å, °).

<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>
O1w—H1 $\cdots$ Cl1	0.85 (1)	2.37 (1)	3.216 (1)	177 (2)

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

We thank Zhengzhou University and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2148).

## References

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**supplementary materials**

*Acta Cryst.* (2010). E66, o1211 [ doi:10.1107/S1600536810015096 ]

## 1,1'-Methylenedipyridinium dichloride monohydrate

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### Comment

Dichloromethane reacts with tertiary amines under high pressure to form bis-ammonium salts, as exemplified by its reaction with pyridine (Almarzoqi *et al.*, 1986). This class of compounds represents a class of ammonium salts that are excellent directing reagents for the construction of metal–organic architectures (Niu *et al.*, 2008). The structure of the dipyridiniummethane dichloride homolog has not been reported but the structure of the anhydrous diiodide has been known for some time. The salt shows short cation–iodine contacts [3.620 (7)–3.742 (9) Å], which are believed to render the salt useful for studying charge-transfer processes in the solid state (Brüdgam & Hartl, 1986). Dipyridiniummethane dichloride crystallizes as a dihydrate (Scheme I, Fig. 1). The dication lies about a two-fold rotation axis that passes through the methylene carbon atom [N–C–N 110.2 (2) °]; the water molecule also lies on a two-fold rotation axis; the molecule is hydrogen–bond donor to the chlorine atom.

### Experimental

The compound was synthesized as described by Almarzoqi *et al.* (1986). The attempt to react it with CuI and [NH<sub>4</sub>]<sub>2</sub>[WO<sub>2</sub>S<sub>2</sub>] in a methanol-DMF mixture, returned the salt as rice-bead shaped yellow crystals.

### Refinement

Hydrogen atoms were placed in calculated positions (C–H 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation, with  $U(H)$  set to  $1.2U_{eq}(C)$ . The water H-atom was located in a difference Fourier map, and was refined with a restraint of O–H 0.84±0.01 Å.

### Figures

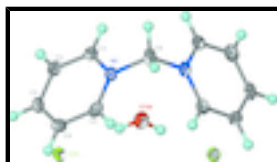


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of [C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>]<sup>2+</sup>·2Cl<sup>−</sup>·H<sub>2</sub>O at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

## 1,1'-Methylenedipyridinium dichloride monohydrate

### Crystal data

C<sub>11</sub>H<sub>12</sub>N<sub>2</sub><sup>2+</sup>·2Cl<sup>−</sup>·H<sub>2</sub>O

$M_r = 261.14$

Orthorhombic, *Fdd2*

$F(000) = 1088$

$D_x = 1.427 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

# supplementary materials

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Hall symbol: F2 -2d  
 $a = 16.3384$  (15) Å  
 $b = 19.0958$  (18) Å  
 $c = 7.7916$  (7) Å  
 $V = 2430.9$  (4) Å<sup>3</sup>  
 $Z = 8$

Cell parameters from 2704 reflections  
 $\theta = 3.1$ – $28.2^\circ$   
 $\mu = 0.51$  mm<sup>-1</sup>  
 $T = 100$  K  
Bead, yellow  
 $0.30 \times 0.15 \times 0.10$  mm

## Data collection

Bruker SMART APEX  
diffractometer  
Radiation source: fine-focus sealed tube  
graphite  
 $\omega$  scans  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.861$ ,  $T_{\max} = 0.950$   
5641 measured reflections

1389 independent reflections  
1333 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 27.4^\circ$ ,  $\theta_{\text{min}} = 3.1^\circ$   
 $h = -21 \rightarrow 21$   
 $k = -23 \rightarrow 24$   
 $l = -10 \rightarrow 10$

## Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.056$   
 $S = 1.03$   
1389 reflections  
78 parameters  
2 restraints  
Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map  
Hydrogen site location: inferred from neighbouring  
sites  
H atoms treated by a mixture of independent and  
constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 1.2206P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983), 642 Friedel pairs  
Flack parameter: 0.01 (6)

## Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.12462 (2)	0.17275 (2)	0.49998 (5)	0.01587 (10)	
O1W	0.2500	0.2500	0.2443 (2)	0.0215 (3)	
H1	0.2178 (13)	0.2280 (11)	0.311 (3)	0.045 (7)*	
N1	0.18673 (8)	0.21731 (7)	-0.11511 (17)	0.0151 (3)	
C1	0.19934 (9)	0.15212 (8)	-0.0531 (2)	0.0166 (3)	
H1A	0.2490	0.1283	-0.0780	0.020*	
C2	0.14070 (9)	0.12028 (8)	0.0456 (2)	0.0179 (3)	
H2	0.1495	0.0744	0.0892	0.021*	
C3	0.06819 (9)	0.15569 (8)	0.0813 (2)	0.0181 (3)	
H3	0.0272	0.1345	0.1503	0.022*	

C4	0.05662 (9)	0.22220 (8)	0.0150 (2)	0.0206 (3)	
H4	0.0072	0.2468	0.0373	0.025*	
C5	0.11688 (10)	0.25259 (9)	-0.0834 (2)	0.0185 (3)	
H5	0.1093	0.2983	-0.1289	0.022*	
C6	0.2500	0.2500	-0.2232 (3)	0.0204 (5)	
H6A	0.2754	0.2141	-0.2978	0.024*	0.50
H6B	0.2246	0.2859	-0.2978	0.024*	0.50

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.01387 (14)	0.01789 (17)	0.01585 (16)	-0.00100 (12)	0.00111 (14)	0.00074 (14)
O1W	0.0237 (8)	0.0210 (8)	0.0199 (9)	-0.0049 (6)	0.000	0.000
N1	0.0153 (6)	0.0175 (6)	0.0127 (6)	-0.0044 (5)	0.0002 (5)	-0.0016 (5)
C1	0.0141 (7)	0.0166 (7)	0.0191 (8)	-0.0001 (6)	-0.0005 (6)	-0.0034 (6)
C2	0.0184 (7)	0.0149 (8)	0.0204 (8)	-0.0012 (6)	-0.0016 (6)	0.0001 (6)
C3	0.0153 (7)	0.0222 (8)	0.0166 (8)	-0.0065 (6)	0.0019 (6)	-0.0034 (7)
C4	0.0150 (6)	0.0207 (7)	0.0261 (9)	0.0011 (6)	0.0001 (7)	-0.0066 (7)
C5	0.0183 (8)	0.0154 (8)	0.0219 (9)	-0.0013 (6)	-0.0067 (6)	-0.0025 (7)
C6	0.0199 (10)	0.0282 (12)	0.0131 (11)	-0.0111 (9)	0.000	0.000

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1W—H1	0.85 (1)	C3—C4	1.384 (2)
N1—C5	1.348 (2)	C3—H3	0.9500
N1—C1	1.351 (2)	C4—C5	1.376 (2)
N1—C6	1.4724 (18)	C4—H4	0.9500
C1—C2	1.371 (2)	C5—H5	0.9500
C1—H1A	0.9500	C6—N1 <sup>i</sup>	1.4724 (18)
C2—C3	1.392 (2)	C6—H6A	0.9900
C2—H2	0.9500	C6—H6B	0.9900
C5—N1—C1	121.60 (14)	C5—C4—C3	119.82 (14)
C5—N1—C6	119.16 (12)	C5—C4—H4	120.1
C1—N1—C6	119.22 (12)	C3—C4—H4	120.1
N1—C1—C2	120.18 (15)	N1—C5—C4	119.80 (16)
N1—C1—H1A	119.9	N1—C5—H5	120.1
C2—C1—H1A	119.9	C4—C5—H5	120.1
C1—C2—C3	119.44 (15)	N1 <sup>i</sup> —C6—N1	110.20 (18)
C1—C2—H2	120.3	N1 <sup>i</sup> —C6—H6A	109.6
C3—C2—H2	120.3	N1—C6—H6A	109.6
C4—C3—C2	119.15 (14)	N1 <sup>i</sup> —C6—H6B	109.6
C4—C3—H3	120.4	N1—C6—H6B	109.6
C2—C3—H3	120.4	H6A—C6—H6B	108.1
C5—N1—C1—C2	-0.4 (2)	C1—N1—C5—C4	0.3 (2)
C6—N1—C1—C2	-178.98 (14)	C6—N1—C5—C4	178.89 (16)
N1—C1—C2—C3	0.0 (2)	C3—C4—C5—N1	0.2 (2)
C1—C2—C3—C4	0.5 (2)	C5—N1—C6—N1 <sup>i</sup>	97.68 (14)

## supplementary materials

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C2—C3—C4—C5                      -0.6 (2)

C1—N1—C6—N1<sup>i</sup>

-83.73 (13)

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

### *Hydrogen-bond geometry (Å, °)*

*D*—H $\cdots$ *A*

*D*—H

H $\cdots$ *A*

*D* $\cdots$ *A*

*D*—H $\cdots$ *A*

O1w—H1 $\cdots$ Cl1

0.85 (1)

2.37 (1)

3.216 (1)

177 (2)

Fig. 1

