Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,1′-Methylenedipyridinium dichloride monohydrate

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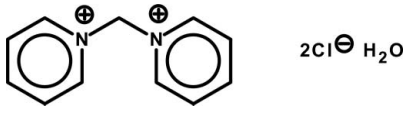
Received 20 April 2010; accepted 24 April 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–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, $C_{11}H_{12}N_2^{2+}\cdot 2Cl^-\cdot H_2O$, the dication adopts a butterfly shape [dihedral angle between rings = 69.0 (1)°] 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···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 dipyridiniomethane 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

$C_{11}H_{12}N_2^{2+}\cdot 2Cl^-\cdot H_2O$
M_r = 261.14
Orthorhombic, *Fdd*2
a = 16.3384 (15) Å
b = 19.0958 (18) Å
c = 7.7916 (7) Å
V = 2430.9 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.51 mm^{-1}
T = 100 K
0.30 × 0.15 × 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_{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^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Absolute structure: Flack (1983), 642 Friedel pairs
Flack parameter: 0.01 (6)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1···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: *publCIF* (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

Almarzoqi, B., George, A. V. & Isaacs, N. S. (1986). *Tetrahedron*, **42**, 601–607.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Brüdgam, I. & Hartl, H. (1986). *Acta Cryst.* C**42**, 866–868.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Niu, Y. Y., Wu, B. L., Guo, X. L., Song, Y. L., Liu, X. C., Zhang, H. Y., Hou, H. W., Niu, C. Y. & Ng, S. W. (2008). *Cryst. Growth Des.* **8**, 2393–2401.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supporting information

Acta Cryst. (2010). E**66**, o1211 [https://doi.org/10.1107/S1600536810015096]

1,1′-Methylenedipyridinium dichloride monohydrate

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S1. 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 regents for the construction of metal–organic architectures (Niu *et al.*, 2008). The structure of the dipyridiniomethane 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 studing charge-transfer processes in the solid state (Brüdgam & Hartl, 1986). Dipyridiniomethane 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 chorine atom.

S2. Experimental

The compound was synthesized as described by Almarzoqi *et al.* (1986). The attempt to react it with CuI and $[NH_4]_2[WO_2S_2]$ in a methanol-DMF mixture. returned the salt as rice-bead shaped yellow crystals.

S3. 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.

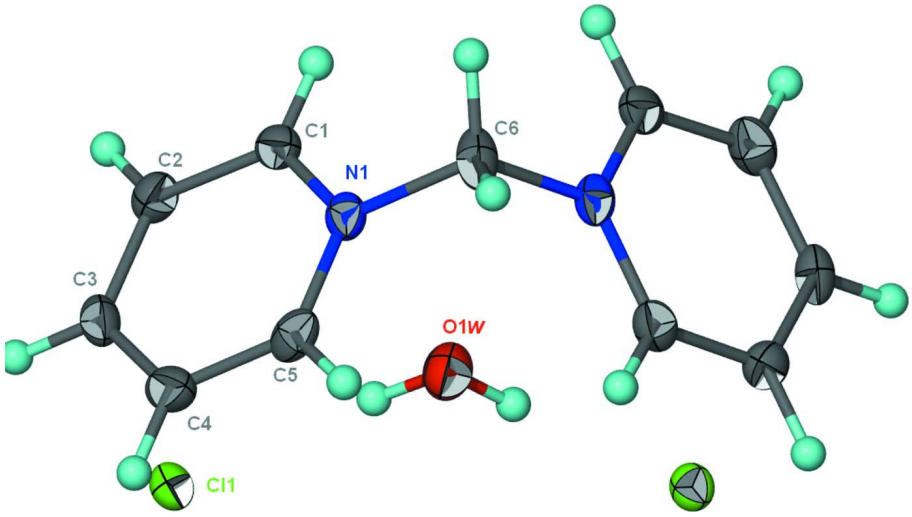

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $[C_{11}H_{12}N_2]^{2+}$ $2Cl^{-}\cdot H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

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Crystal data

$C_{11}H_{12}N_2^{2+}\cdot 2Cl^{-}\cdot H_2O$
$M_r = 261.14$
Orthorhombic, *Fdd*2
Hall symbol: F2 -2d
$a = 16.3384\ (15)$ Å
$b = 19.0958\ (18)$ Å
$c = 7.7916\ (7)$ Å
$V = 2430.9\ (4)$ Å^3
$Z = 8$
$F(000) = 1088$
$D_x = 1.427$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2704 reflections
$\theta = 3.1–28.2°$
$\mu = 0.51$ mm^{-1}
$T = 100$ K
Bead, yellow
0.30 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω 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 $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.1°$
$h = -21\rightarrow21$
$k = -23\rightarrow24$
$l = -10\rightarrow10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.056$
$S = 1.04$
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Absolute structure: Flack (1983), 642 Friedel pairs
Absolute structure parameter: 0.01 (6)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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 (Å, º)

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^{i}	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^{i}—C6—N1	110.20 (18)
C1—C2—H2	120.3	N1^{i}—C6—H6A	109.6
C3—C2—H2	120.3	N1—C6—H6A	109.6
C4—C3—C2	119.15 (14)	N1^{i}—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^{i}	97.68 (14)
C2—C3—C4—C5	−0.6 (2)	C1—N1—C6—N1^{i}	−83.73 (13)

Symmetry code: (i) −*x*+1/2, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1w—H1···Cl1	0.85 (1)	2.37 (1)	3.216 (1)	177 (2)