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1-Hydroxy-4-methylpyridinium chloride

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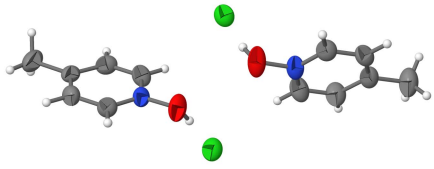
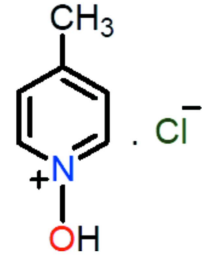
Structural data: full structural data are available from iucrdata.iucr.org

The title salt, $C_6H_8NO^+\cdot Cl^-$, contains two cations and two anions in the asymmetric unit. The components are linked by O—H···Cl and C—H···Cl hydrogen bonds, leading to tetra- (square-planar) or penta-coordinated (square-pyramidal) chloride ions. The title salt is isostructural with its bromide analogue.

3D view



Chemical scheme



Structure description

The title molecular salt, $C_6H_8NO^+\cdot Cl^-$, **1**, crystallizes with two 1-hydroxy-4-methylpyridinium cations and two chloride anions in the asymmetric unit in space group $P2_1/c$, indicating that proton transfer has occurred from HCl to the *N*-oxide O atoms (Fig. 1). The N—O bond lengths are 1.371 (2) and 1.379 (2) Å, which are comparable to its bromide analogue **2** (1.373 and 1.374 Å; Ryzhakova *et al.*, 2012). The average N—O—H bond angle in **1** [103.9 (19)°] is significantly smaller compared to **2** (110.9°). However, the torsion angles C_{Ar}—N—O—H in **1** (62.9 and 57.4°) are very similar to those in **2** (62.8 and 57.6°).

In the extended structure of **1**, one of the cations provides four hydrogen-bond donors (three C—H groupings and one O—H group) while the other cation provides five hydrogen-bond donors, *i.e.*, one from the O—H group and four from C—H centres, all with chloride ion acceptors to form tetra/penta-coordinated anions (Table 1; Fig. 2). As expected, the H···Cl separation for the O—H···Cl hydrogen bonds (mean 1.97 Å) is much shorter than the H···Cl separation for the C—H···Cl hydrogen bonds (mean 2.79 Å).

Synthesis and crystallization

A 2.0 *M* solution of hydrochloric acid in Et_2O (0.167 ml, 5.49 mmol) was added dropwise to an ethanol (3 ml) solution of 4-methylpyridine *N*-oxide (0.2 g, 1.83 mmol). The reaction scheme is shown in Fig. 3. The reaction mixture was stirred for 2 h at room

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···Cl2	0.86 (3)	2.03 (3)	2.8847 (19)	175 (3)
O2—H2A···Cl1	0.98 (3)	1.91 (3)	2.879 (2)	172 (3)
C2—H2···Cl1^{i}	0.93	2.81	3.567 (2)	139
C5—H5···Cl1	0.93	2.73	3.519 (2)	143
C7—H7···Cl2	0.93	2.79	3.652 (3)	154
C8—H8···Cl1^{ii}	0.93	2.72	3.618 (3)	162
C10—H10···Cl1^{iii}	0.93	2.81	3.672 (2)	155
C11—H11···Cl2^{iv}	0.93	2.74	3.646 (2)	164

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z$; (iv) $x, y, z-1$.

temperature followed by solvent evaporation using a rotary evaporator to obtain a solid. The obtained product was washed with diethyl ether and dried to get colorless solid. Yield: 82%, m.p. 114°C. ^{1}H NMR (500 MHz, $CDCl_3$, p.p.m.) δ 8.81 (*d*, 2H, J = 6.5 Hz), 7.70 (*d*, 2H, J = 6.5 Hz), 2.62 (*s*, 3H). ^{1}H NMR (CD_3OD, 500 MHz, p.p.m.): δ 8.70 (*d*, 2H, J = 6.5 Hz), 7.96 (*d*, 2H, J = 6 Hz), 2.70 (*s*, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, p.p.m.): 154.0, 138.9, 128.5, 21.7.

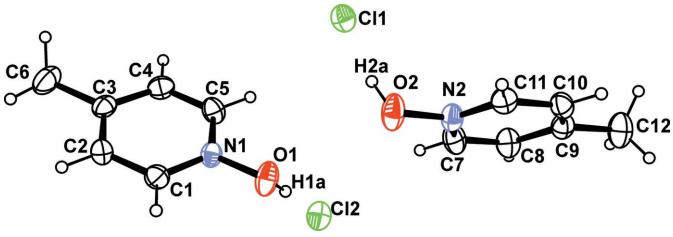


Figure 1
ORTEP diagram of **1** with 50% displacement ellipsoid probability level.

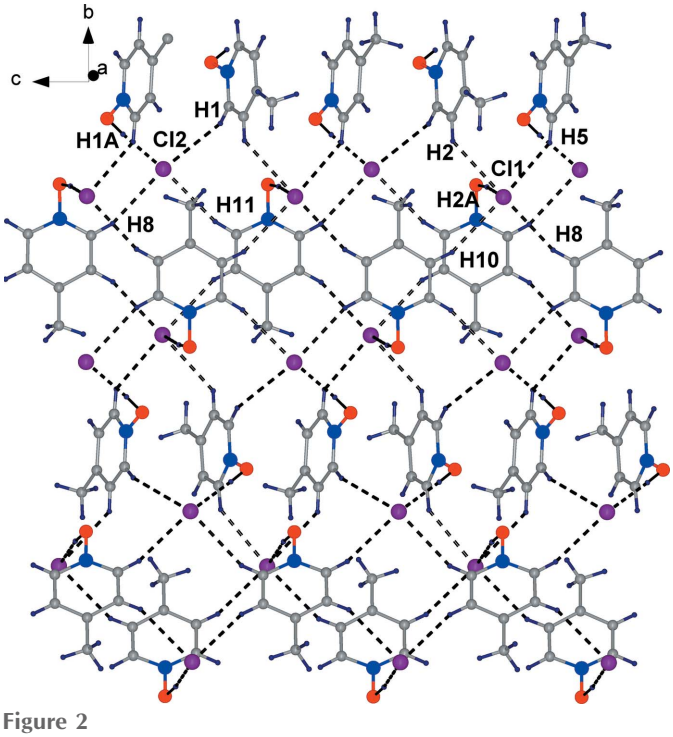


Figure 2
Two-dimensional packing diagram of **1**.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_8NO^+\cdot Cl^-$
M_r	145.58
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	7.1610 (16), 26.271 (6), 7.7474 (17)
β (°)	95.495 (3)
V (Å^3)	1450.8 (6)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.44
Crystal size (mm)	0.11 × 0.09 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.953, 0.974
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	41123, 3354, 2663
R_{int}	0.051
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.129, 1.06
No. of reflections	3354
No. of parameters	171
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.26

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

The slow evaporation of a dichloromethane solution of **1** produced good quality, pale-yellow, rhombus-shaped crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

We thank IIT Kanpur for Single-crystal XRD data collection and CURaj for infrastructure facilities. Authors contributions are as follows. Conceptualization, RT; methodology, AS, KD and RT; investigation, RT; writing (original draft), AS; writing (review and editing of the manuscript), RT; visualization, RT; funding acquisition, RT; resources, RT; supervision, RT.

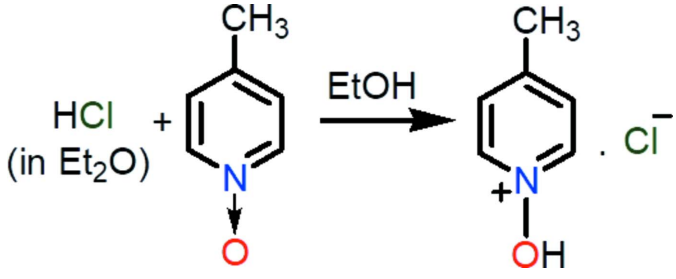


Figure 3
Reaction scheme.

Funding information

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full crystallographic data

IUCrData (2022). **7**, x221023 [https://doi.org/10.1107/S2414314622010239]

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Crystal data

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M_r = 145.58
Monoclinic, $P2_1/c$
a = 7.1610 (16) Å
b = 26.271 (6) Å
c = 7.7474 (17) Å
β = 95.495 (3)°
V = 1450.8 (6) Å^3
Z = 8
$F(000)$ = 608
D_x = 1.333 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9290 reflections
θ = 2.8–24.5°
μ = 0.44 mm^{-1}
T = 296 K
Needle, colorless
0.11 × 0.09 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.953, T_{max} = 0.974
41123 measured reflections
3354 independent reflections
2663 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.6°, θ_{min} = 1.6°
h = −9→9
k = −34→34
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.129
S = 1.06
3354 reflections
171 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.4782P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3022 (3)	0.78000 (7)	0.4800 (3)	0.0457 (4)
H1	0.400319	0.800303	0.449620	0.055*
C2	0.1436 (3)	0.80150 (8)	0.5313 (3)	0.0500 (5)
H2	0.133207	0.836765	0.534577	0.060*
C3	−0.0028 (3)	0.77163 (8)	0.5785 (2)	0.0448 (4)
C4	0.0191 (3)	0.71936 (8)	0.5702 (3)	0.0496 (5)
H4	−0.075402	0.698063	0.602249	0.060*
C5	0.1785 (3)	0.69878 (8)	0.5152 (3)	0.0488 (5)
H5	0.191540	0.663677	0.506589	0.059*
C6	−0.1788 (3)	0.79546 (12)	0.6313 (3)	0.0711 (7)
H6A	−0.166953	0.831849	0.629104	0.107*
H6B	−0.283357	0.785194	0.552116	0.107*
H6C	−0.198791	0.784606	0.746382	0.107*
C7	0.6459 (3)	0.54962 (9)	0.3558 (3)	0.0571 (5)
H7	0.608047	0.564925	0.454901	0.069*
C8	0.7375 (3)	0.50418 (9)	0.3661 (3)	0.0564 (5)
H8	0.761757	0.488208	0.472987	0.068*
C9	0.7952 (3)	0.48143 (8)	0.2181 (3)	0.0485 (5)
C10	0.7595 (3)	0.50710 (8)	0.0630 (3)	0.0477 (5)
H10	0.799599	0.493306	−0.037661	0.057*
C11	0.6660 (3)	0.55255 (8)	0.0555 (3)	0.0477 (5)
H11	0.641024	0.569680	−0.049225	0.057*
C12	0.8943 (4)	0.43125 (10)	0.2289 (4)	0.0741 (7)
H12A	0.905880	0.419521	0.346807	0.111*
H12B	0.823683	0.406943	0.156757	0.111*
H12C	1.016852	0.435067	0.190073	0.111*
N1	0.3148 (2)	0.72972 (6)	0.47417 (19)	0.0405 (4)
N2	0.6116 (2)	0.57173 (6)	0.2021 (2)	0.0474 (4)
CL1	0.15453 (8)	0.58405 (2)	0.27982 (7)	0.05342 (17)
CL2	0.59963 (8)	0.64306 (2)	0.69818 (7)	0.05963 (19)
O1	0.4730 (2)	0.70951 (7)	0.4144 (2)	0.0599 (4)
O2	0.5160 (3)	0.61737 (6)	0.1905 (3)	0.0670 (5)
H1A	0.517 (4)	0.6892 (11)	0.495 (4)	0.084 (10)*
H2A	0.393 (4)	0.6090 (12)	0.228 (4)	0.088 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0450 (10)	0.0393 (10)	0.0525 (11)	−0.0037 (8)	0.0041 (8)	0.0030 (8)
C2	0.0510 (11)	0.0393 (10)	0.0586 (12)	0.0063 (8)	0.0000 (9)	−0.0050 (9)
C3	0.0394 (9)	0.0594 (12)	0.0348 (9)	0.0058 (8)	−0.0009 (7)	−0.0047 (8)
C4	0.0439 (10)	0.0559 (12)	0.0493 (11)	−0.0069 (9)	0.0056 (8)	0.0053 (9)
C5	0.0588 (12)	0.0363 (10)	0.0524 (11)	−0.0026 (8)	0.0114 (9)	0.0003 (8)
C6	0.0472 (12)	0.099 (2)	0.0664 (15)	0.0218 (12)	0.0036 (11)	−0.0100 (14)
C7	0.0726 (14)	0.0504 (12)	0.0525 (12)	0.0004 (10)	0.0271 (10)	−0.0030 (10)

C8	0.0690 (14)	0.0532 (12)	0.0494 (12)	0.0051 (10)	0.0174 (10)	0.0066 (10)
C9	0.0457 (10)	0.0430 (10)	0.0585 (12)	−0.0016 (8)	0.0146 (9)	0.0006 (9)
C10	0.0516 (11)	0.0458 (11)	0.0476 (11)	−0.0038 (9)	0.0145 (9)	−0.0070 (9)
C11	0.0477 (10)	0.0474 (11)	0.0492 (11)	−0.0048 (8)	0.0116 (8)	0.0034 (9)
C12	0.0871 (19)	0.0566 (14)	0.0821 (18)	0.0209 (13)	0.0252 (14)	0.0068 (13)
N1	0.0429 (8)	0.0426 (8)	0.0373 (8)	0.0066 (7)	0.0097 (6)	−0.0004 (6)
N2	0.0494 (9)	0.0346 (8)	0.0616 (10)	0.0001 (7)	0.0216 (8)	0.0019 (7)
CL1	0.0606 (3)	0.0456 (3)	0.0555 (3)	−0.0034 (2)	0.0130 (2)	0.0013 (2)
CL2	0.0654 (4)	0.0611 (4)	0.0534 (3)	0.0105 (3)	0.0104 (2)	0.0046 (2)
O1	0.0613 (9)	0.0643 (10)	0.0585 (9)	0.0200 (8)	0.0288 (8)	0.0073 (8)
O2	0.0717 (11)	0.0387 (8)	0.0967 (13)	0.0096 (7)	0.0401 (9)	0.0097 (8)

Geometric parameters (Å, º)

C1—N1	1.325 (3)	C7—H7	0.9300
C1—C2	1.361 (3)	C8—C9	1.390 (3)
C1—H1	0.9300	C8—H8	0.9300
C2—C3	1.386 (3)	C9—C10	1.380 (3)
C2—H2	0.9300	C9—C12	1.495 (3)
C3—C4	1.384 (3)	C10—C11	1.367 (3)
C3—C6	1.499 (3)	C10—H10	0.9300
C4—C5	1.367 (3)	C11—N2	1.335 (3)
C4—H4	0.9300	C11—H11	0.9300
C5—N1	1.332 (3)	C12—H12A	0.9600
C5—H5	0.9300	C12—H12B	0.9600
C6—H6A	0.9600	C12—H12C	0.9600
C6—H6B	0.9600	N1—O1	1.371 (2)
C6—H6C	0.9600	N2—O2	1.379 (2)
C7—N2	1.326 (3)	O1—H1A	0.86 (3)
C7—C8	1.361 (3)	O2—H2A	0.98 (3)
N1—C1—C2	118.98 (19)	C7—C8—H8	119.7
N1—C1—H1	120.5	C9—C8—H8	119.7
C2—C1—H1	120.5	C10—C9—C8	117.57 (19)
C1—C2—C3	121.03 (19)	C10—C9—C12	121.8 (2)
C1—C2—H2	119.5	C8—C9—C12	120.7 (2)
C3—C2—H2	119.5	C11—C10—C9	120.85 (19)
C4—C3—C2	117.21 (18)	C11—C10—H10	119.6
C4—C3—C6	122.0 (2)	C9—C10—H10	119.6
C2—C3—C6	120.8 (2)	N2—C11—C10	118.36 (19)
C5—C4—C3	120.56 (19)	N2—C11—H11	120.8
C5—C4—H4	119.7	C10—C11—H11	120.8
C3—C4—H4	119.7	C9—C12—H12A	109.5
N1—C5—C4	119.06 (19)	C9—C12—H12B	109.5
N1—C5—H5	120.5	H12A—C12—H12B	109.5
C4—C5—H5	120.5	C9—C12—H12C	109.5
C3—C6—H6A	109.5	H12A—C12—H12C	109.5
C3—C6—H6B	109.5	H12B—C12—H12C	109.5

H6A—C6—H6B	109.5	C1—N1—C5	123.14 (17)
C3—C6—H6C	109.5	C1—N1—O1	117.29 (16)
H6A—C6—H6C	109.5	C5—N1—O1	119.49 (16)
H6B—C6—H6C	109.5	C7—N2—C11	123.68 (18)
N2—C7—C8	118.9 (2)	C7—N2—O2	119.18 (17)
N2—C7—H7	120.5	C11—N2—O2	117.14 (18)
C8—C7—H7	120.5	N1—O1—H1A	104 (2)
C7—C8—C9	120.6 (2)	N2—O2—H2A	103.9 (18)
N1—C1—C2—C3	0.6 (3)	C12—C9—C10—C11	178.9 (2)
C1—C2—C3—C4	−0.4 (3)	C9—C10—C11—N2	0.6 (3)
C1—C2—C3—C6	−178.7 (2)	C2—C1—N1—C5	0.4 (3)
C2—C3—C4—C5	−0.8 (3)	C2—C1—N1—O1	177.09 (18)
C6—C3—C4—C5	177.5 (2)	C4—C5—N1—C1	−1.6 (3)
C3—C4—C5—N1	1.8 (3)	C4—C5—N1—O1	−178.24 (18)
N2—C7—C8—C9	0.4 (4)	C8—C7—N2—C11	−1.7 (3)
C7—C8—C9—C10	1.3 (3)	C8—C7—N2—O2	178.9 (2)
C7—C8—C9—C12	−179.4 (2)	C10—C11—N2—C7	1.2 (3)
C8—C9—C10—C11	−1.8 (3)	C10—C11—N2—O2	−179.39 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl2	0.86 (3)	2.03 (3)	2.8847 (19)	175 (3)
O2—H2*A*···Cl1	0.98 (3)	1.91 (3)	2.879 (2)	172 (3)
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