2-(Hydroxymethyl)pyridinium chloride

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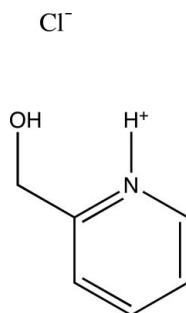Correspondence e-mail: laottle@sandia.gov

In the title molecular salt, $C_6H_8NO^+\cdot Cl^-$, the packing is consolidated by N—H···Cl and O—H···Cl hydrogen bonds, resulting in the formation of [010] chains of alternating cations and anions.

Related literature

The title compound was initially isolated by Boyle *et al.* (2008). Only the di-substituted pyridine carbonyl HCl salt has been reported previously (Fites *et al.*, 2006).

Experimental

Crystal data

$C_6H_8NO^+\cdot Cl^-$	$c = 12.1304$ (16) Å
$M_r = 145.58$	$\beta = 102.078$ (2)°
Monoclinic, $P2_1/n$	$V = 677.79$ (15) Å³
$a = 7.0689$ (9) Å	$Z = 4$
$b = 8.0833$ (11) Å	Mo $K\alpha$ radiation

$\mu = 0.47$ mm⁻¹	$0.25 \times 0.22 \times 0.20$ mm
$T = 173$ (2) K	

Data collection

Bruker APEX CCD area-detector diffractometer	4681 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)	1227 independent reflections
$T_{min} = 0.867$, $T_{max} = 0.909$	1202 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.092$	
$S = 1.26$	$\Delta\rho_{max} = 0.28$ e Å⁻³
1227 reflections	$\Delta\rho_{min} = -0.23$ e Å⁻³
87 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl1ⁱ	0.82	2.24	3.0409 (18)	167
N1—H7···Cl1ⁱⁱ	0.83 (3)	2.34 (3)	3.067 (2)	146 (2)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XSHELL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

References

Boyle, T. J., Ottley, L. M., Rodriguez, M. A., Sewell, R. M., Alam, T. M. & McIntyre, S. K. (2008). *Inorg. Chem.* Submitted.
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supporting information

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S1. Comment

Figure 1 shows an atomic displacement ellipsoid plot of 2(hydroxymethyl)pyridinium chloride. The title compound was synthesized through the dissolution of bis(pyridine carbonoxide)titanium(dichloride), $(OPy)_2TiCl_2$, in $H_2O/HCl(5\%)$. The synthesis was optimized by dissolving HOPy in $H_2O/HCl(5\%)$. Fites, *et al.* (2006) reported the disubstituted salt structure which was isolated from a vanadium 2,6-pyridinedimethanol complex at low pH solutions. This is in agreement to what Boyle *et al.*(2008) found, where the title compound was isolated from low pH aqueous solutions of the titanium monosubstituted pyridinemethanol complex.

Figure 2 displays the packing arrangement of four molecules of the title compound with the Cl···H interactions that occur between adjacent molecules. The Cl interacts with the pyridinium (N1—H7···Cl1) and alcohol protons (O1—H1···Cl1), with a greater interaction observed with the alcohol, as listed in Table 1. The hydrogen bond angles for O1—H1···Cl1 and N1—H7···Cl1 are in agreement with literature angles and intermolecular interactions. In comparison, the disubstituted structure by Fites, *et al.* (2006) showed a stronger Cl binding potential with respect to the pyridinium proton (H···Cl = 2.208 Å) and a slightly weaker interaction with the alcohol (H···Cl 2.37 Å). Figure 2 also displays the pattern of H···Cl bonding throughout the unit cells. The individual molecules are related by a 2_1 screw axis parallel to the *b* axis of the structure. The alternating interaction of the Cl between the pyridinium proton and the alcohol proton yields a intermolecular chain along the *b* axis.

S2. Experimental

2(Hydroxymethyl)pyridinium chloride was isolated by Boyle *et al.*(2008) through the dissolution of a titanium precursor, bis(pyridine carbonoxide)titanium(dichloride) or $(OPy)_2TiCl_2$, (where OPy = pyridine carbonoxide) in acidified water (5% of conc. HCl in water). In order to optimize the synthesis of this salt, crystal were grown *via* HOPy in acidified water (5% of conc. HCl in water). After slow evaporation, X-ray quality crystals were isolated and characterized by single-crystal X-ray, FTIR, NMR, and EA.

S3. Refinement

H1 (which is bound to O1 of the methanol group) was placed on ideal position, allowed to rotate around the C—O bond and refined *via* a riding model while H7 was located on difference Fourier maps and allowed to refine freely.
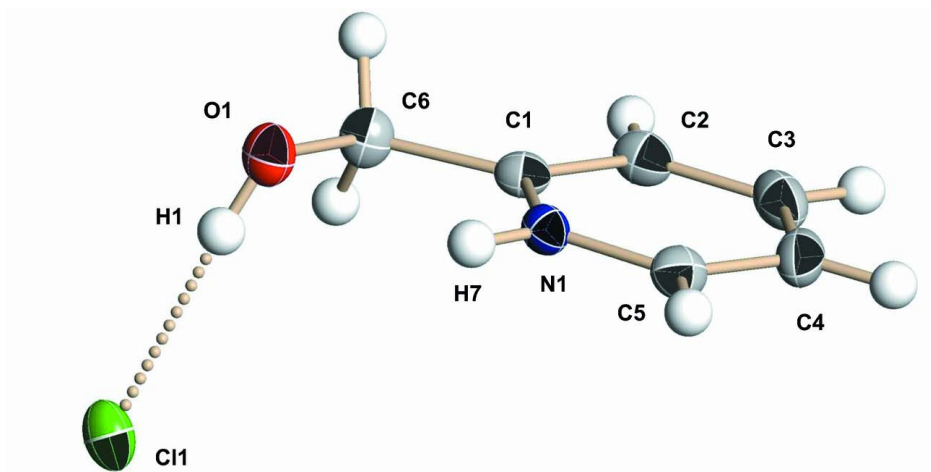
Figure 1

The molecular structure of the title compound, with atom labels and 50% probability atomic displacement ellipsoids for non-H atoms. The Cl atom has been translated to clarify interaction with the OH group.
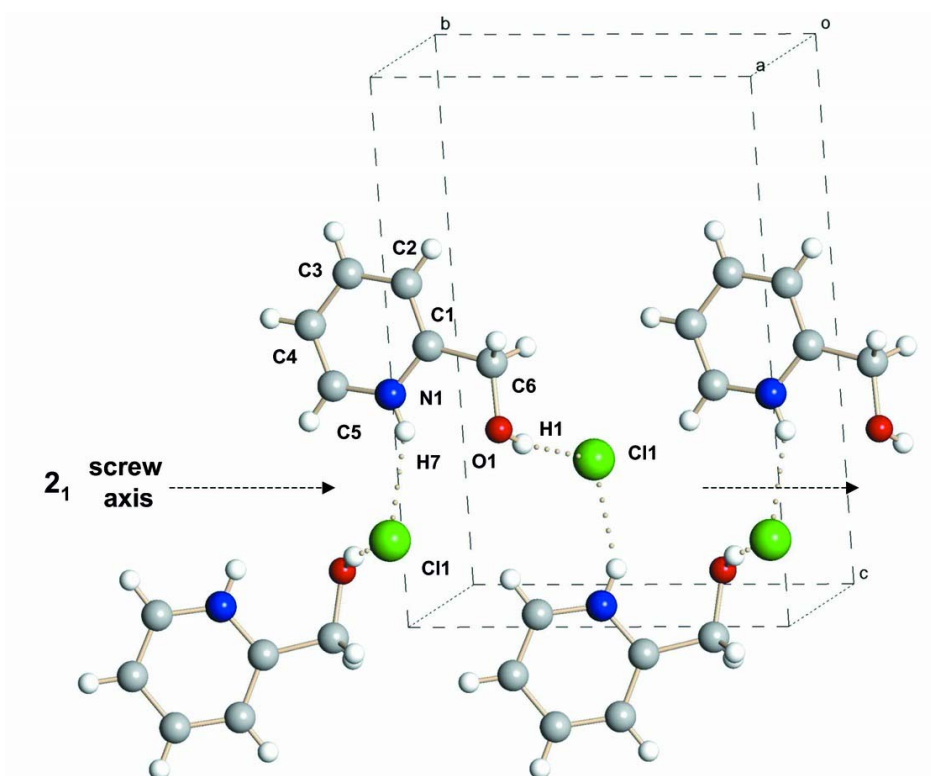
Figure 2

Packing of the title compound on the b-c plane illustrating the NH—Cl—OH intermolecular chain interaction which proceeds parallel to the *b* axis *via* the 2_1 screw axis.

2-(Hydroxymethyl)pyridinium chloride

Crystal data

$C_6H_8NO^+ \cdot Cl^-$	$F(000) = 304$
$M_r = 145.58$	$D_x = 1.427$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 200 reflections
$a = 7.0689$ (9) Å	$\theta = 3.1–25.2°$
$b = 8.0833$ (11) Å	$\mu = 0.48$ mm^{-1}
$c = 12.1304$ (16) Å	$T = 173$ K
$\beta = 102.078$ (2)°	Irregular, colorless
$V = 677.79$ (15) Å^3	$0.25 \times 0.22 \times 0.20$ mm
$Z = 4$	

Data collection

Bruker APEX CCD area-detector diffractometer	4681 measured reflections
	1227 independent reflections
Radiation source: fine-focus sealed tube	1202 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.020$
φ and ω scans	$\theta_{max} = 25.2°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)	$h = -8\rightarrow8$
	$k = -9\rightarrow9$
$T_{min} = 0.867$, $T_{max} = 0.909$	$l = -14\rightarrow13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.093$	
$S = 1.26$	H atoms treated by a mixture of independent and constrained refinement
1227 reflections	
87 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + 0.6606P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.28$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.10702 (9)	0.46272 (7)	0.68760 (4)	0.0311 (2)
N1	0.2053 (3)	0.4526 (2)	−0.05399 (16)	0.0213 (4)
O1	0.0732 (2)	0.1503 (2)	−0.10825 (13)	0.0292 (4)

H1	0.1498	0.1040	−0.1403	0.044*
C1	0.2214 (3)	0.3472 (3)	0.03263 (18)	0.0220 (5)
C4	0.3390 (3)	0.6739 (3)	0.0620 (2)	0.0299 (5)
H4	0.3773	0.7840	0.0715	0.036*
C5	0.2628 (3)	0.6116 (3)	−0.04288 (19)	0.0264 (5)
H5	0.2509	0.6789	−0.1062	0.032*
C3	0.3576 (3)	0.5680 (3)	0.1541 (2)	0.0312 (6)
H3	0.4104	0.6074	0.2260	0.037*
C2	0.2989 (3)	0.4061 (3)	0.14015 (19)	0.0271 (5)
H2	0.3109	0.3364	0.2022	0.033*
C6	0.1592 (3)	0.1715 (3)	0.00685 (18)	0.0273 (5)
H6A	0.2708	0.0993	0.0266	0.033*
H6B	0.0674	0.1402	0.0524	0.033*
H7	0.165 (4)	0.414 (3)	−0.118 (2)	0.027 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0410 (4)	0.0293 (3)	0.0204 (3)	−0.0037 (2)	0.0005 (2)	0.0035 (2)
N1	0.0213 (9)	0.0237 (10)	0.0181 (9)	0.0011 (8)	0.0023 (7)	−0.0017 (8)
O1	0.0326 (9)	0.0303 (9)	0.0229 (8)	−0.0027 (7)	0.0015 (7)	−0.0028 (7)
C1	0.0194 (11)	0.0260 (11)	0.0209 (11)	0.0026 (9)	0.0050 (8)	0.0030 (9)
C4	0.0264 (12)	0.0236 (12)	0.0391 (14)	−0.0003 (10)	0.0052 (10)	−0.0071 (10)
C5	0.0266 (12)	0.0228 (12)	0.0305 (12)	0.0038 (9)	0.0076 (9)	0.0029 (10)
C3	0.0271 (12)	0.0382 (14)	0.0266 (12)	0.0034 (11)	0.0018 (9)	−0.0102 (11)
C2	0.0273 (12)	0.0340 (13)	0.0197 (11)	0.0033 (10)	0.0038 (9)	0.0012 (10)
C6	0.0323 (13)	0.0260 (12)	0.0223 (11)	−0.0020 (10)	0.0026 (9)	0.0028 (9)

Geometric parameters (Å, º)

N1—C1	1.339 (3)	C4—C3	1.392 (4)
N1—C5	1.347 (3)	C4—H4	0.9300
N1—H7	0.83 (3)	C5—H5	0.9300
O1—C6	1.412 (3)	C3—C2	1.372 (3)
O1—H1	0.8200	C3—H3	0.9300
C1—C2	1.389 (3)	C2—H2	0.9300
C1—C6	1.500 (3)	C6—H6A	0.9700
C4—C5	1.370 (3)	C6—H6B	0.9700
C1—N1—C5	123.7 (2)	C2—C3—C4	120.8 (2)
C1—N1—H7	116.8 (18)	C2—C3—H3	119.6
C5—N1—H7	119.3 (18)	C4—C3—H3	119.6
C6—O1—H1	109.5	C3—C2—C1	119.5 (2)
N1—C1—C2	118.1 (2)	C3—C2—H2	120.2
N1—C1—C6	117.76 (19)	C1—C2—H2	120.2
C2—C1—C6	124.2 (2)	O1—C6—C1	111.60 (18)
C5—C4—C3	118.2 (2)	O1—C6—H6A	109.3
C5—C4—H4	120.9	C1—C6—H6A	109.3

C3—C4—H4	120.9	O1—C6—H6B	109.3	
N1—C5—C4	119.7 (2)	C1—C6—H6B	109.3	
N1—C5—H5	120.1	H6A—C6—H6B	108.0	
C4—C5—H5	120.1			

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯Cl1[i]	0.82	2.24	3.0409 (18)	167
N1—H7⋯Cl1[ii]	0.83 (3)	2.34 (3)	3.067 (2)	146 (2)

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