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Pyridinium carbonyl chloride

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Abstract

The crystal structure of the title compound, C_6H_8ClNO, is presented. This salt is composed of the molecule pyridinium carbonyl and a Cl counter-ion. Packing diagrams indicate weak intermolecular interactions between the Cl ion and associated pyridinium and alcohol hydrogen atoms. These interactions result in the formation of NH···Cl···OH···Cl chains which propagate along the *b* axis, dictated by the 2_1 screw axis.

Related literature

Boyle *et al.* (2008) initially isolated the title compound from an acidified water solution (5% of conc. HCl in water) of bis(pyridine carbonoxide)titanium(dichloride), $(OPy)_2TiCl_2$, (where OPy = pyridine carbonoxide). The compound was then successfully synthesized directly through the dissolution of H-OPy in an acidified water solution. Only the di-substituted pyridine carbonyl HCl salt has been previously reported (Fites, *et al.*; 2006).

Computing details

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

(8nv301s)

Crystal data

C_6H_8ClNO	$V = 677.79\ (15)$ Å^3
$M_r = 145.58$	$Z = 4$
Monoclinic, $P2(1)/n$	Mo $K\alpha$
$a = 7.0689\ (9)$ Å	$\mu = 0.48$ mm^{-1}
$b = 8.0833\ (11)$ Å	$T = 273\ (2)$ K

c = 12.1304 (16) Å	0.25 × 0.22 × 0.20 mm
β = 102.078 (2)º	

Data collection

CCD area detector diffractometer	1227 independent reflections
Absorption correction: empirical (using intensity measurements) SADABS (Sheldrick, 1999)	1202 reflections with $I > 2\sigma(I)$
T_{min} = 0.867, T_{max} = 0.909	R_{int} = 0.020
4681 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$wR(F^2)$ = 0.093	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
S = 1.26	Absolute structure: ?
1227 reflections	Flack parameter: ?
87 parameters	Rogers parameter: ?
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bond geometry (Å, °)

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.

Acknowledgements

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supplementary materials

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Comment

Figure 1 shows an atomic displacement ellipsoid plot of pyridinium carbonyl chloride, hereafter referred to as compound (I). (I) was synthesized through the dissolution of bis(pyridine carbonoxide)titanium(dichloride),$(OPy)_2TiCl_2$, in H_2O/HCl(5%). The synthesis of (I) 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 monosubsituted pyridinemethanol complex.

Figure 2 displays the packing arrangement of four molecules of (I) with the Cl—H interactions that occur between adjacent molecules. The Cl interaction with the pyridinium (Cl1—H7—N1) has a Cl—H bond distance of 2.34 (3) Å while the Cl interaction with the alcohol (Cl1—H1—O1) displays a shorter bond distance of Cl1—H1 = 2.24 Å. The hydrogen bond angle for the Cl1—H1—O1 was 166.9° and that of the Cl1—H7—N1 measured at 146 (2)° are reasonable for these type of intermolecular interactions. In comparison, the disubtituted structure by Fites, *et al.* (2006) showed a stronger Cl binding potential with respect to the pyridinium proton (Cl—H = 2.208 Å) and a slightly weaker interaction with the alcohol (Cl—H 2.37 Å).

Figure 3 shows packing arrangement along *b* axis. This figure displays the pattern of Cl—H 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 (I) along the *b* axis.

Experimental

Pyridinium carbonyl chloride was isolated by Boyle *et al.*(2008) through the dissolution of a titanium precursor, $(OPy)_2TiCl_2$, 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.

Figures

Figure 1. The molecular structure of (I), 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 (I) as viewed down the *b* axis illustrating the Cl—H interactions *via* OH and NH of the pyridinium carbonyl molecule.
Figure 3. View of the b-c plane of (I) to illustrate the OH—Cl—HN intermolecular chain interaction which proceeds parallel to the *b* axis *via* the 2_1 screw axis.

(8nv301s)

Crystal data

C_6H_8ClNO	F_{000} = 304
M_r = 145.58	D_x = 1.427 Mg m^{-3}
Monoclinic, $P2(1)/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 2836 reflections
a = 7.0689 (9) Å	θ = 3.1–25.2º
b = 8.0833 (11) Å	μ = 0.48 mm^{-1}
c = 12.1304 (16) Å	T = 273 (2) K
β = 102.078 (2)º	Irregular, colorless
V = 677.79 (15) Å^3	0.25 × 0.22 × 0.20 mm
Z = 4	

Data collection

CCD area detector diffractometer	1227 independent reflections
Radiation source: fine-focus sealed tube	1202 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.020
T = 273(2) K	θ_{max} = 25.2º
phi and ω scans	θ_{min} = 3.1º
Absorption correction: empirical (using intensity measurements) SADABS (Sheldrick, 1999)	h = −8→8
T_{min} = 0.867, T_{max} = 0.909	k = −9→9
4681 measured reflections	l = −14→13

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.040	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.093	$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + 0.6606P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.26	$(\Delta/\sigma)_{max} < 0.001$
1227 reflections	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
87 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 (Å^2)

	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, °)

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, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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