

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(4-Chlorophenyl)methanaminium chloride hemihydrate

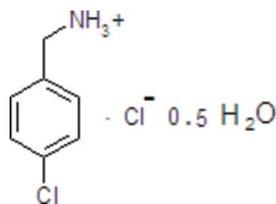
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Received 1 June 2010; accepted 2 June 2010

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.048; wR factor = 0.130; data-to-parameter ratio = 41.7.

In the title hydrated salt, $\text{C}_7\text{H}_9\text{ClN}^+\cdot\text{Cl}^- \cdot 0.5\text{H}_2\text{O}$, the water O atom lies on a crystallographic twofold axis. In the crystal, the monoprotonated 4-chlorobenzylammonium cation forms $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and the water molecule forms $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds, generating layers lying parallel to the bc plane.

Related literature

 For the properties of benzylamines, see: Markwardt *et al.* (2005). For a related structure, see: Dhaouadi *et al.* (2008).


Experimental

Crystal data

 $\text{C}_7\text{H}_9\text{ClN}^+\cdot\text{Cl}^- \cdot 0.5\text{H}_2\text{O}$
 $M_r = 187.06$
 Monoclinic, $C2/c$
 $a = 30.462$ (2) Å

 $b = 4.890$ (3) Å
 $c = 11.738$ (2) Å
 $\beta = 99.97$ (3)°
 $V = 1722.1$ (11) Å³
 $Z = 8$
 Ag $K\alpha$ radiation
 $\lambda = 0.56085$ Å

 $\mu = 0.35$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

 Enraf–Nonius TurboCAD-4 diffractometer
 5908 measured reflections
 4207 independent reflections

 2217 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 2 standard reflections every 120 min
 intensity decay: 5%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.130$
 $S = 1.00$
 4207 reflections
 101 parameters

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}-\text{H0A}\cdots\text{Cl1}^{\text{i}}$	0.89	2.60	3.2930 (19)	136
$\text{N}-\text{H0A}\cdots\text{Cl1}^{\text{ii}}$	0.89	2.78	3.417 (2)	130
$\text{N}-\text{H0B}\cdots\text{O}$	0.89	2.04	2.866 (2)	155
$\text{N}-\text{H0C}\cdots\text{Cl1}^{\text{iii}}$	0.89	2.26	3.144 (2)	175
$\text{O}-\text{H1}\cdots\text{Cl1}$	0.85 (3)	2.28 (3)	3.1230 (18)	171 (3)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5481).

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supporting information

Acta Cryst. (2010). E66, o1627 [doi:10.1107/S1600536810021100]

(4-Chlorophenyl)methanaminium chloride hemihydrate

Sofiane Souissi, Wajda Smirani Sta, Salem S. Al-Deyab and Mohamed Rzaigui

S1. Comment

Derivatives of benzylamine were found to be competitive inhibitors of the proteolytic enzymes trypsin, plasmin, and thrombin. So, the 4-chlorobenzylamine is a strong thrombin inhibitor but only of low effectiveness against trypsin and plasmin for the hydrolysis of N- α -benzoyl catalyzed by these three enzymes. Relations between the chemical structure and the activity against trypsin, plasmin and thrombin were deduced by comparing the inhibitor constants (Markwardt, F. *et al.*, 2005). In this work, we report the crystal structure of the title compound (I). As shown in (Fig.1), the asymmetric unit of (I) is built up from one 4-chlorobenzylammonium cation, one chloride anion and one water molecule. The Cl⁻ anions, water molecules and R—NH₃⁺ groups are linked *via* O—H \cdots Cl, N—H \cdots O and N—H \cdots Cl hydrogen bonds and ionic interactions, so as to built inorganic layers spreading around the (b,c) planes. The 4-chlorobenzylammonium cations are anchored onto the successive inorganic layers *via* hydrogen bonds and electrostatic interactions, to composite their negative charges.

The examination of the organic cation shows that the values of N—C, C—C, C—Cl distances and N—C—C, C—C—C, C—C—Cl angles range from 1.376 (3) to 1.736 (3) Å and 115.72 (19) to 122.80 (19)°, respectively. These values show no significant difference from those obtained in other organic materials associated with the same organic groups (Dhaouadi, H. *et al.*, 2008).

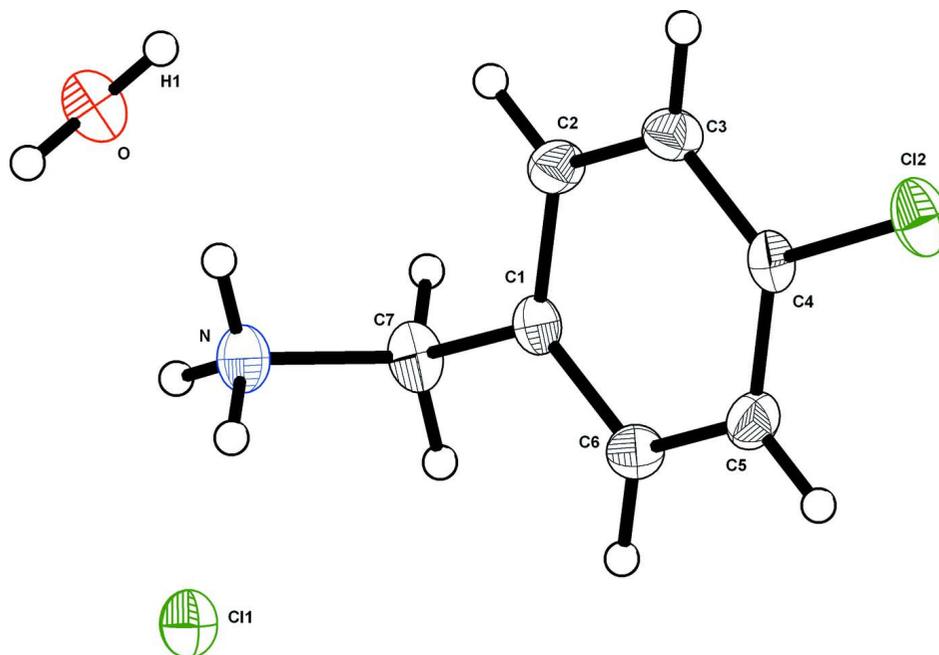
In this structure, the water molecules play a very important role in the cohesion of the various groups. It participates with the organic cations and chloride anions in the H-bonding scheme of N—H \cdots O and O—H \cdots Cl interactions in the crystal structure. The four hydrogen bonds are relatively weak, and their donor acceptor distances vary from 2.866 (2) to 3.417 (3) Å. Thus, these different interactions (hydrogen bonds, Van der Waals, and electrostatic) form a stable three-dimensional network.

S2. Experimental

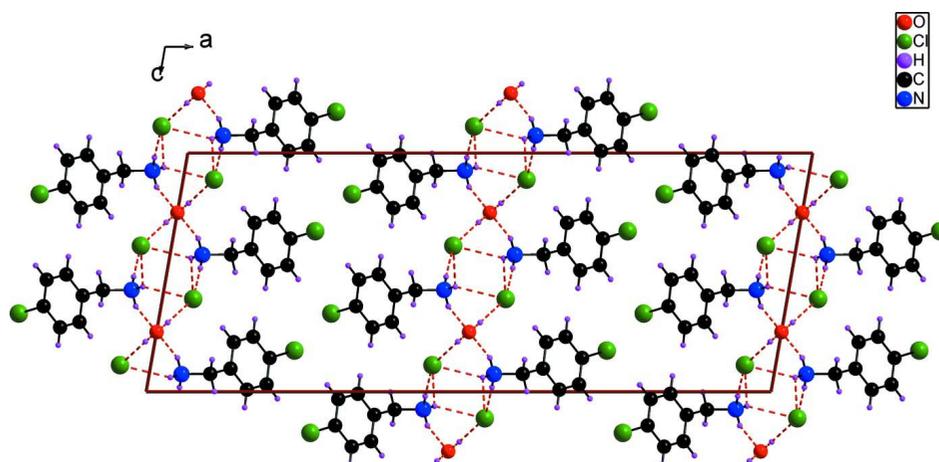
An ethanolic solution of 4-chlorobenzylamine (10 mmol, in 10 ml) was added, with stirring, to 20 ml of an aqueous HCl solution (0.5M) at room temperature. Colourless blocks of (I) were obtained on slow evaporation of the solvent.

S3. Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms, [N—H = 0.89, C—H = 0.96 Å (CH₃) with with $U_{\text{iso}}(\text{H}) = 1.5\text{Ueq}$ and C—H = 0.96 Å (Ar—H), with $U_{\text{iso}}(\text{H}) = 1.5\text{Ueq}$], but those attached to oxygen atom are located in a difference map


Figure 1

View of (I) with displacement ellipsoids for non-H atoms are drawn at the 30% probability level.


Figure 2

A view of the packing of (I) along the *b* axis.

(4-Chlorophenyl)methanaminium chloride hemihydrate

Crystal data

$C_7H_9ClN^+ \cdot Cl^- \cdot 0.5H_2O$

$M_r = 187.06$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 30.462(2) \text{ \AA}$

$b = 4.890(3) \text{ \AA}$

$c = 11.738(2) \text{ \AA}$

$\beta = 99.97(3)^\circ$

$V = 1722.1(11) \text{ \AA}^3$

$Z = 8$

$F(000) = 776$

$D_x = 1.443 \text{ Mg m}^{-3}$

Ag $K\alpha$ radiation, $\lambda = 0.56085 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9\text{--}11^\circ$

$\mu = 0.35 \text{ mm}^{-1}$

$T = 293$ K $0.30 \times 0.25 \times 0.20$ mm
 Block, colourless

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	$R_{\text{int}} = 0.031$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$
Graphite monochromator	$h = -50 \rightarrow 50$
non-profiled ω scans	$k = 0 \rightarrow 8$
5908 measured reflections	$l = -5 \rightarrow 19$
4207 independent reflections	2 standard reflections every 120 min
2217 reflections with $I > 2\sigma(I)$	intensity decay: 5%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.2911P]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4207 reflections	$\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
101 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0080 (12)
Secondary atom site location: difference Fourier map	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.049348 (13)	0.63727 (9)	0.11132 (4)	0.04257 (13)
O	0.0000	0.2285 (4)	0.2500	0.0494 (5)
H1	0.0151 (8)	0.323 (5)	0.210 (2)	0.089 (9)*
C1	0.12851 (4)	0.0280 (3)	0.40289 (14)	0.0313 (3)
C2	0.12629 (5)	0.1317 (3)	0.29253 (14)	0.0364 (3)
H2	0.1048	0.0661	0.2328	0.044*
C3	0.15582 (5)	0.3328 (3)	0.26977 (14)	0.0371 (3)
H3	0.1538	0.4046	0.1957	0.045*
C4	0.18814 (4)	0.4244 (3)	0.35851 (14)	0.0329 (3)
C5	0.19059 (5)	0.3278 (4)	0.46938 (15)	0.0386 (4)
H5	0.2121	0.3947	0.5289	0.046*
C6	0.16065 (5)	0.1293 (4)	0.49129 (14)	0.0380 (3)

H6	0.1621	0.0631	0.5661	0.046*
C7	0.09748 (5)	-0.1977 (3)	0.42512 (18)	0.0399 (4)
H7A	0.0966	-0.3362	0.3656	0.048*
H7B	0.1090	-0.2824	0.4990	0.048*
Cl2	0.225682 (14)	0.66901 (9)	0.32754 (5)	0.04948 (15)
N	0.05166 (4)	-0.0999 (3)	0.42641 (13)	0.0404 (3)
H0A	0.0347	-0.2400	0.4401	0.061*
H0B	0.0406	-0.0261	0.3582	0.061*
H0C	0.0521	0.0251	0.4817	0.061*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0390 (2)	0.0365 (2)	0.0527 (3)	0.00140 (16)	0.00925 (17)	0.00195 (19)
O	0.0523 (11)	0.0428 (10)	0.0574 (12)	0.000	0.0215 (9)	0.000
C1	0.0289 (6)	0.0260 (6)	0.0403 (8)	0.0011 (5)	0.0097 (6)	-0.0002 (6)
C2	0.0372 (7)	0.0376 (8)	0.0333 (8)	-0.0070 (6)	0.0033 (6)	-0.0044 (7)
C3	0.0441 (8)	0.0367 (8)	0.0314 (8)	-0.0060 (7)	0.0086 (6)	0.0008 (7)
C4	0.0281 (6)	0.0281 (6)	0.0444 (9)	-0.0017 (5)	0.0117 (6)	-0.0042 (6)
C5	0.0318 (7)	0.0436 (9)	0.0388 (9)	-0.0035 (6)	0.0011 (6)	-0.0064 (7)
C6	0.0388 (7)	0.0407 (8)	0.0342 (8)	0.0015 (7)	0.0057 (6)	0.0049 (7)
C7	0.0384 (7)	0.0263 (7)	0.0577 (11)	0.0010 (6)	0.0153 (7)	0.0043 (7)
Cl2	0.0432 (2)	0.0391 (2)	0.0709 (3)	-0.01276 (17)	0.0229 (2)	-0.0055 (2)
N	0.0339 (6)	0.0355 (7)	0.0529 (9)	-0.0069 (5)	0.0101 (6)	0.0005 (6)

Geometric parameters (Å, °)

O—H1	0.84 (2)	C5—C6	1.386 (2)
C1—C2	1.382 (2)	C5—H5	0.9300
C1—C6	1.389 (2)	C6—H6	0.9300
C1—C7	1.505 (2)	C7—N	1.4779 (19)
C2—C3	1.389 (2)	C7—H7A	0.9700
C2—H2	0.9300	C7—H7B	0.9700
C3—C4	1.379 (2)	N—H0A	0.8900
C3—H3	0.9300	N—H0B	0.8900
C4—C5	1.374 (2)	N—H0C	0.8900
C4—Cl2	1.7361 (15)		
C2—C1—C6	118.89 (14)	C5—C6—C1	120.84 (15)
C2—C1—C7	120.10 (15)	C5—C6—H6	119.6
C6—C1—C7	120.98 (15)	C1—C6—H6	119.6
C1—C2—C3	120.78 (15)	N—C7—C1	112.77 (13)
C1—C2—H2	119.6	N—C7—H7A	109.0
C3—C2—H2	119.6	C1—C7—H7A	109.0
C4—C3—C2	119.10 (15)	N—C7—H7B	109.0
C4—C3—H3	120.5	C1—C7—H7B	109.0
C2—C3—H3	120.5	H7A—C7—H7B	107.8
C5—C4—C3	121.21 (14)	C7—N—H0A	109.5

C5—C4—C12	120.36 (12)	C7—N—H0B	109.5
C3—C4—C12	118.42 (13)	H0A—N—H0B	109.5
C4—C5—C6	119.14 (14)	C7—N—H0C	109.5
C4—C5—H5	120.4	H0A—N—H0C	109.5
C6—C5—H5	120.4	H0B—N—H0C	109.5

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N—H0A...C11 ⁱ	0.89	2.60	3.2930 (19)	136
N—H0A...C11 ⁱⁱ	0.89	2.78	3.417 (2)	130
N—H0B...O	0.89	2.04	2.866 (2)	155
N—H0C...C11 ⁱⁱⁱ	0.89	2.26	3.144 (2)	175
O—H1...C11	0.85 (3)	2.28 (3)	3.1230 (18)	171 (3)

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