

O-(2,3,4,5,6-Pentafluorobenzyl)hydroxyl-
aminium chloride

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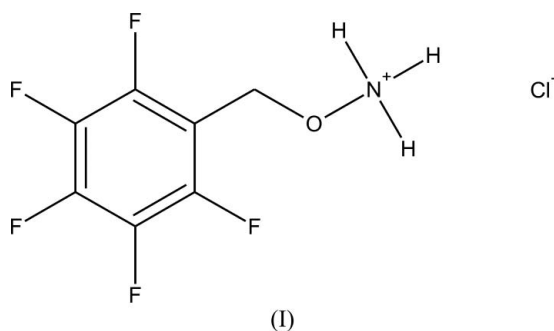
Key indicators

Single-crystal X-ray study
 $T = 130$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.039
 wR factor = 0.090
Data-to-parameter ratio = 11.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{C}_7\text{H}_5\text{F}_5\text{NO}^+\cdot\text{Cl}^-$, consists of two-dimensional networks of hydrogen-bonded primary NH_3^+ cations and chloride anions with the pentafluorobenzyl moieties located on one side of the layer. To maximize the Coulombic interactions, the Cl^- anions approach the NH_3^+ groups of the neighbouring network along the O—N bond direction [$\text{O}-\text{N}\cdots\text{Cl} = 174.3(2)^\circ$]. The $\text{N}\cdots\text{Cl}$ distance between the ions belonging to two adjacent networks is $3.066(2)$ Å and is shorter than the $\text{N}\cdots\text{Cl}$ distances in the $\text{N}^+-\text{H}\cdots\text{Cl}^-$ hydrogen bonds [$3.099(3)$ – $3.133(3)$ Å].

Comment

Primary ammonium halides are known to assemble in crystal structures *via* $\text{N}^+-\text{H}\cdots\text{Cl}^-$ hydrogen bonds into ladders, cubanes and two-dimensional networks fully utilizing the hydrogen-bonding ability of the RNH_3^+ group (Gray & Jones, 2002*a,b*; Lopez-Dupla *et al.*, 2003; Bond, 2005). Besides hydrogen bonds, to maximize Coulombic interactions within the crystal structure, ammonium groups and halide anions often form additional short $\text{N}^+\cdots\text{Cl}^-$ contacts (Bond, 2005).



Our interest in the title compound, (I), originates from recent reports on the interactions between anions and electron-deficient π -acidic rings (Quiñonero *et al.*, 2002; Garau, Frontera *et al.*, 2003; Garau, Quiñonero *et al.*, 2003; Domesheko *et al.*, 2004). Quiñonero *et al.* (2002) provided computational evidence for non-bonding interactions between hexafluorobenzene and several anions and found 27 structures in the Cambridge Structural Database (Allen, 2002) where the interaction of anions with pentafluorobenzene derivatives could be postulated. By solving the crystal structure of (I), we aimed to investigate whether the pentafluorophenyl moiety is able to compete for Coulombic interactions with the NH_3^+ group. We expected that in (I) the ammonium group attached *via* a flexible $-\text{CH}_2-\text{O}-$ arm to a pentafluorophenyl ring should co-operate with the aromatic ring in the anion binding.

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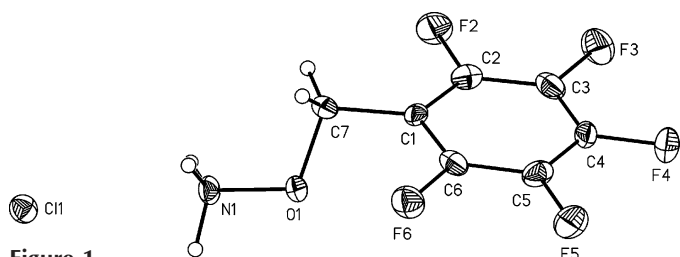


Figure 1
View of the asymmetric unit of (I), shown with 50% displacement ellipsoids.

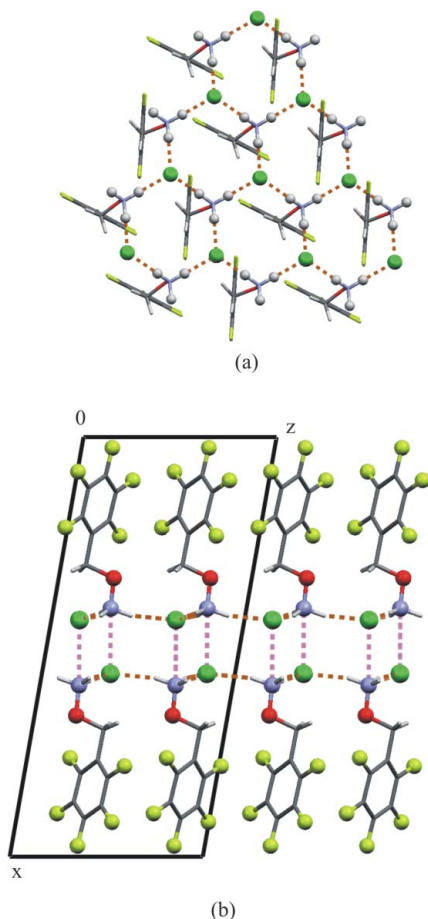


Figure 2
The crystal structure of (I), showing (a) the hydrogen-bonded layer of cations and anions parallel to the (100) plane and (b) the arrangement of two layers in the crystal structure. Hydrogen bonds are shown as brown dashed lines and short $\text{N}^+\cdots\text{Cl}^-$ interlayer contacts as violet dashed lines.

The structure of (I), with its atom numbering, is shown in Fig. 1. Analysis of the crystal packing revealed that the postulated anion- π ring interactions do not exist in (I). Primary ammonium groups and chloride anions form three $\text{N}^+-\text{H}\cdots\text{Cl}^-$ hydrogen bonds (Table 1), generating two-dimensional networks composed of R_6^3 motifs (Fig. 2a). The six-membered rings of the network have a very flattened chair conformation. The pentafluorobenzyl moieties are grouped on one side of the layer, resulting in its polar structure. A similar polar two-dimensional assembly was observed in anilinium chloride (Lopez-Dupla *et al.*, 2003) and is rather exceptional among ammonium halides (Bond, 2005). However, there is a

striking difference between the two structures. Crystals of anilinium chloride are polar, *i.e.* adjacent layers are in contact *via* their hydrophilic and hydrophobic faces. In (I), the Coulombic attraction between oppositely charged units located on the hydrophilic side of the layer leads to a centrosymmetric structure (Fig. 2b). To maximize the Coulombic interactions, the Cl^- anions approach the NH_3^+ groups of the neighbouring network along the cation O-N bond direction [$\text{O}-\text{N}\cdots\text{Cl} = 174.3(2)^\circ$]. The $\text{N}\cdots\text{Cl}$ distance between the two networks is $3.066(2) \text{ \AA}$ and is shorter than the $\text{N}\cdots\text{Cl}$ distances of the $\text{N}^+-\text{H}\cdots\text{Cl}^-$ hydrogen bonds [$3.099(3)$ – $3.133(3) \text{ \AA}$].

Experimental

The title compound was purchased from Aldrich and recrystallized from ethanol [m.p. 500 K (sublimation)].

Crystal data

$\text{C}_7\text{H}_5\text{F}_5\text{NO}^+\cdot\text{Cl}^-$
 $M_r = 249.57$
 Monoclinic, $P2_1/c$
 $a = 19.994(3) \text{ \AA}$
 $b = 5.4020(8) \text{ \AA}$
 $c = 9.0305(15) \text{ \AA}$
 $\beta = 99.939(13)^\circ$
 $V = 960.7(3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.725 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 2766 reflections
 $\theta = 4-25^\circ$
 $\mu = 0.45 \text{ mm}^{-1}$
 $T = 130(2) \text{ K}$
 Needle, colourless
 $0.42 \times 0.12 \times 0.03 \text{ mm}$

Data collection

Kuma KM4CCD κ -geometry diffractometer
 ω scans
 Absorption correction: none
 3889 measured reflections
 1702 independent reflections

1042 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -23 \rightarrow 23$
 $k = -6 \rightarrow 6$
 $l = -10 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.090$
 $S = 0.90$
 1702 reflections
 148 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{Cl1}^i$	0.98 (4)	2.15 (4)	3.107 (3)	165 (3)
$\text{N1}-\text{H1B}\cdots\text{Cl1}^{ii}$	1.01 (3)	2.11 (3)	3.099 (3)	166 (2)
$\text{N1}-\text{H1C}\cdots\text{Cl1}^{iii}$	1.02 (4)	2.11 (4)	3.133 (3)	177 (3)

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

All H atoms were located in electron-density difference maps. The C-H bond distances were standardized to 0.97 \AA and these H atoms were then refined as riding. Positional parameters of H atoms from the NH_3^+ group and isotropic displacement parameters of all H atoms were allowed to refine.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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