2-(Methoxycarbonyl)anilinium chloride monohydrate

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The asymmetric unit of the title compound, $C_8H_{10}NO_2^+\cdot Cl^-\cdot H_2O$, contains two crystallographically independent 2-(methoxycarbonyl)anilinium cations related by a pseudo-inversion centre, two chloride ions and two water molecules. A three-dimensional network structure is formed via N—H$\cdots$O, N—H$\cdots$Cl and O—H$\cdots$Cl hydrogen bonds, and π–π stacking interactions.

Comment

Methyl 2-aminobenzoate is used as an intermediate for fine chemicals (Zhang, 1992). It is known that many esters of 2-aminobenzoate display a broad range of biological activities (Li *et al.*, 1998). Synthetic esters of 2-aminobenzoate show useful properties (Ye, 2000). Furthermore, these esters can also be used as interesting ligands. These properties stimulated us to find new methods to synthesize them and study their structures and activities. We report here the crystal structure of the title compound, (I).

(I)
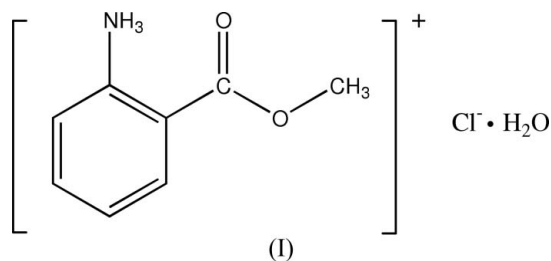
The asymmetric unit contains two crystallographically independent methyl 2-aminobenzoate cations related by a pseudo-inversion centre, two chloride ions and two water molecules (Fig. 1). The corresponding bond lengths and angles in the independent methyl 2-aminobenzoate molecules agree with each other (Table 1) and show normal values. The N1- and N2-containing cations are each essentially planar, with r.m.s. deviations of 0.074 and 0.045 Å, respectively. In the crystal structure, the molecules are linked together via N—H$\cdots$O and N—H$\cdots$Cl hydrogen bonds involving the amine groups, and by O—H$\cdots$Cl hydrogen bonds, to form a three-dimensional network. In addition, the crystal packing is stabilized by weak π–π interactions resulting from the stacking of inversion-related C9–C14 benzene rings along the *a* axis. The $Cg\cdots Cg^v$ and $Cg\cdots Cg^{vi}$ distances are 3.781 (1) and 3.725 (1) Å, respectively, where Cg is the centroid of the C9–C14 benzene ring [symmetry codes: (v) $-x$, $2 - y$, $1 - z$; (vi) $1 - x$, $2 - y$, $1 - z$]; similar features are observed in related structures (Du *et al.*, 2003; Jin & Xiao, 2005).
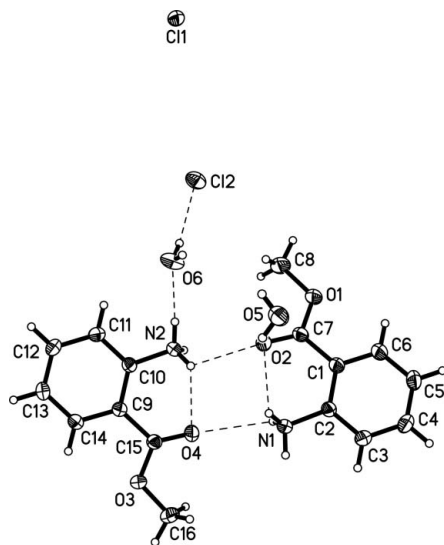
Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines represent hydrogen bonds.
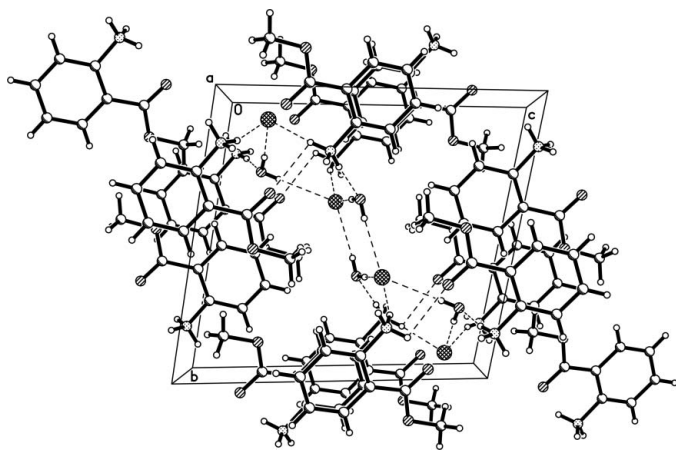
Figure 2
Packing diagram for (I). The hydrogen bonds are indicated by dashed lines.

Experimental

Compound (I) was synthesized according to a literature procedure (Dan, 2000). Single crystals suitable for X-ray measurements were grown from a solution in methanol at room temperature by slow evaporation.

Crystal data

$C_8H_{10}NO_2{}^+ \cdot Cl^- \cdot H_2O$	$Z = 4$
$M_r = 205.64$	$D_x = 1.364$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.4709\ (9)$ Å	Cell parameters from 3522
$b = 11.6988\ (14)$ Å	reflections
$c = 12.3883\ (15)$ Å	$\theta = 2.4–25.7°$
$\alpha = 96.299\ (2)°$	$\mu = 0.36$ mm^{-1}
$\beta = 101.097\ (2)°$	$T = 292\ (2)$ K
$\gamma = 106.844\ (2)°$	Block, colourless
$V = 1001.0\ (2)$ Å^3	$0.32 \times 0.30 \times 0.30$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	3867 independent reflections
	3433 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.016$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 26.0°$
	$h = -9 \rightarrow 8$
$T_{min} = 0.894$, $T_{max} = 0.900$	$k = -14 \rightarrow 14$
5444 measured reflections	$l = -15 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0779P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.2162P]$
$wR(F^2) = 0.128$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
3867 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
255 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

C1—C7	1.488 (3)	C9—C15	1.490 (2)
C2—N1	1.458 (2)	C10—N2	1.458 (2)
C7—O2	1.193 (2)	C15—O4	1.192 (2)
C7—O1	1.326 (2)	C15—O3	1.330 (2)
C8—O1	1.457 (3)	C16—O3	1.450 (2)
O2—C7—O1	123.30 (17)	O3—C15—C9	112.10 (15)
O1—C7—C1	112.60 (16)	C7—O1—C8	115.31 (17)
O4—C15—O3	123.32 (16)	C15—O3—C16	115.88 (15)
C2—C1—C7—O2	7.6 (3)	C14—C9—C15—O3	−2.7 (2)
C6—C1—C7—O1	9.4 (3)	O2—C7—O1—C8	1.6 (3)
C10—C9—C15—O4	−0.5 (3)	C9—C15—O3—C16	178.72 (17)

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1A$\cdots$Cl1^i	0.89	2.33	3.2163 (16)	176
N1—H1B$\cdots$O4	0.89	2.59	2.915 (2)	102
N1—H1B$\cdots$O5^{ii}	0.89	1.89	2.770 (3)	170
N1—H1C$\cdots$O2	0.89	2.35	2.677 (2)	102
N1—H1C$\cdots$Cl1^{iii}	0.89	2.38	3.2459 (17)	163
N2—H2A$\cdots$Cl2^{iv}	0.89	2.31	3.1700 (17)	163
N2—H2B$\cdots$O2	0.89	2.50	2.801 (2)	100
N2—H2B$\cdots$O4	0.89	2.29	2.699 (2)	108
N2—H2B$\cdots$Cl1^{iii}	0.89	2.51	3.3534 (17)	159
N2—H2C$\cdots$O6	0.89	1.91	2.801 (3)	175
O5—H5A$\cdots$Cl2^{iii}	0.78 (3)	2.52 (4)	3.295 (2)	173 (3)
O5—H5B$\cdots$Cl1^{iii}	0.84 (3)	2.38 (4)	3.216 (2)	172 (3)
O6—H6A$\cdots$Cl2^{iii}	0.83 (4)	2.37 (5)	3.188 (2)	172 (4)
O6—H6B$\cdots$Cl2	0.78 (3)	2.41 (3)	3.177 (2)	169 (4)

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

The water H atoms were located in a difference Fourier map and refined isotropically [O—H = 0.78 (3)–0.84 (3) Å]. All other H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C,N—H distances of 0.93 (aromatic), 0.96 (methyl) and 0.89 Å (amino). The $U_{iso}(H)$ values were set equal to $1.2U_{eq}$(carrier) for the aromatic H atoms and to $1.5U_{eq}$(carrier) for methyl and protonated amine H atoms. A rotating-group model was used for the methyl and amine groups.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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