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5-Ammoniosalicylic Acid Chloride Monohydrate

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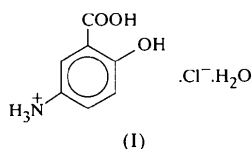
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Abstract

The title compound, $C_7H_8NO_3^+ \cdot Cl^- \cdot H_2O$, crystallized in the centrosymmetric space group $P2_1/c$ in an ionic form, the proton from HCl having been transferred to the amino N atom. The three H atoms on N, the H atom on the carboxyl group, the H atom of the hydroxyl group and the H atoms of the water molecule, all of which are involved in hydrogen bonding, are ordered. The eight 'best' hydrogen bonds have the following donor–acceptor distances: $O \cdots O$ 2.681 (2) and 2.598 (2); $O \cdots Cl$ 3.367 (1), 3.345 (2) and 3.156 (2); $N \cdots O$ 2.995 (2); $N \cdots Cl$ 3.173 (2) and 3.114 (2) Å. In this structure, the acid cations are not linked directly to each other by hydrogen bonds, but are linked indirectly, *via* hydrogen bonds involving chloride ions and water molecules, into a three-dimensional network. Through basic second-level graphs, finite patterns substantially outnumber chains and rings.

Comment

This report on 5-ammoniosalicylic acid chloride monohydrate is one of a series on hydrogen bonding in amino-substituted carboxylic acids (Dobson & Gerkin, 1996, 1998). The title acid crystallized in the centrosymmetric space group $P2_1/c$ in an ionic form, (I), the proton from HCl having been transferred to the N atom. The



refined organic cation, and the chloride anion and water molecule associated with it by the atom list, are shown in Fig. 1, together with the numbering scheme. In this structure, the acid cations are not linked directly to each other by hydrogen bonds, but are linked indirectly *via* hydrogen bonds involving the chloride

anions and water molecules. All the potential conventional hydrogen-bonding H atoms (H1, H2, H1N, H2N, H3N, H1O and H2O) are involved in hydrogen bonds and all are ordered. Geometric details of the 14 hydrogen bonds satisfying our usual criteria ($D \cdots O_{\text{acceptor}} < 3.3$ Å and $H \cdots A < D \cdots A$; also, $D \cdots Cl_{\text{acceptor}} < 3.4$ Å) are given in Table 2. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) involving the eight 'best' hydrogen bonds, which involve each H atom listed above at least once and which are labeled *a–h* in the order given in Table 2, are given in Table 3 for the first- and basic second-level graph sets. The tabulation shows that, although both chains and rings are present, finite patterns are by far the most abundant. In the order in which they are tabulated, the chains propagate along **b**, **b** and **c**. Each of the rings is disposed about a center of symmetry. The basic third-level graph which involves hydrogen bonds *a*, *c* and *g* has the descriptor $C_3^2(10)$, and is a chain propagating in the *a* direction. Since the organic cation has atoms involved in chains propagating in the *a*, *b* and *c* directions, it is clearly involved in a three-dimensional network. It may be noted that there is one C—H—Cl array, namely, $C4—H4 \cdots Cl1^{viii}$ [symmetry code: (viii) $-1 + x, y, z$] with $C4 \cdots Cl = 3.616$ (2) Å and $C4—H \cdots Cl = 151$ (1)°, whose parameters fall well within the Taylor & Kennard (1982) criteria for significantly attractive interactions, recognizing that here Cl represents a chloride ion.

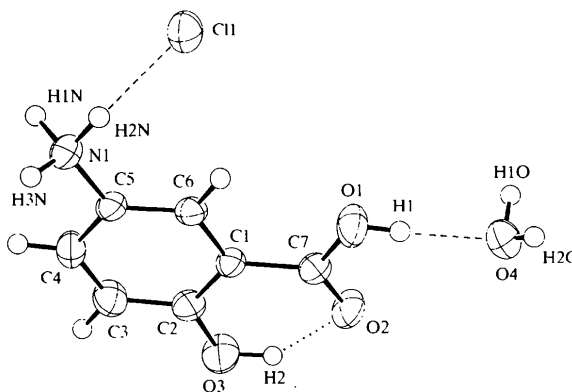


Fig. 1. ORTEP (Johnson, 1976) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small. Intermolecular hydrogen bonds are shown by dashed lines and the intramolecular hydrogen bond by a dotted line.

In this structure the benzene ring is very nearly planar: the maximum deviation of the ring C atoms from the best-fit plane describing them is 0.008 (2) Å, the average deviation 0.005 (2) Å. The dihedral angle

between the two sets of non-parallel ring planes is only $3.85(6)^\circ$. Thus, all the ring planes are virtually parallel. The dihedral angle between the carboxyl group plane (C7, O1, O2) and the ring plane is $2.7(1)^\circ$. Further, the 11 non-H atoms of the organic cation lie nearly in a plane: the maximum deviation of any of these atoms from the best-fit plane describing them is $0.047(1) \text{ \AA}$ (O2).

Distances and angles of special interest in the organic cation are given in Table 1; all distances and angles fall within normal ranges. The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen bonded to each other or in the C4—H4...Cl1 interaction, are not less than the sum of the corresponding Bondi (1964) radii by as much as their s.u.'s. This is unusual among the structures we have determined.

The structure of 4-ammoniosalicylic acid chloride (4ASAC; Lin *et al.*, 1978) affords a number of comparisons with the present structure, although the absence of water obviously changes the overall hydrogen-bonding scheme significantly. The geometries of the non-H atoms of the carboxyl and hydroxyl groups are in good agreement, within the lower precision of the 4ASAC study. In particular, the O1—C7—O2 angles (present nomenclature) are $118.9(9)$ and $122.2(2)^\circ$, while the C1—C2—O3 angles are $122.2(8)$ and $122.9(2)^\circ$, for 4ASAC and (I), respectively. In 4ASAC, the dihedral angle between the best-fit ring plane and the carboxyl group plane is $3.5(10)^\circ$, a value very similar to that cited above for (I). Further, in 4ASAC, as in (I), the 11 non-H atoms of the organic cation lie nearly in a plane: the maximum deviation in 4ASAC of any of these atoms from the best-fit plane describing them is $0.088(8) \text{ \AA}$, and again the deviation is due to O2. With respect to hydrogen bonding, 4ASAC and (I) are similar, in that neither forms carboxylic acid dimers, and each has an intramolecular hydrogen bond involving the hydroxyl group and O2 from the carboxyl group. Furthermore, the N1...Cl1 hydrogen-bonding distances are comparable: $3.162(8)$, $3.171(7)$ and $3.209(8) \text{ \AA}$ in 4ASAC, and $3.114(2)$ and $3.173(2) \text{ \AA}$ in (I). (All values cited for 4ASAC are calculated by us from the published data.)

Experimental

5-Aminosalicylic acid was obtained as a tan granular powder from the Aldrich Chemical Company. This solid was dissolved in aqueous sodium bicarbonate at room temperature and the solution was acidified with hydrochloric acid to pH 1. Room-temperature evaporation of the resulting solution produced columns, one of which was cut to provide the experimental sample.

Crystal data

$\text{C}_7\text{H}_8\text{NO}_3^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$
 $M_r = 207.61$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic
 $P2_1/c$
 $a = 8.044(1) \text{ \AA}$
 $b = 17.093(1) \text{ \AA}$
 $c = 6.949(1) \text{ \AA}$
 $\beta = 105.92(1)^\circ$
 $V = 918.8(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.501 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Rigaku AFC-5S diffractometer
 ω scans
Absorption correction: none
2294 measured reflections
2125 independent reflections
1750 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

Refinement on F^2
 $R(F) = 0.036$
 $wR(F^2) = 0.057$
 $S = 2.98$
2125 reflections
159 parameters
All H-atom parameters refined
 $w = 1/\sigma^2(F^2)$
 $(\Delta/\sigma)_{\text{max}} < 0.01$

Cell parameters from 25 reflections
 $\theta = 15.1\text{--}17.5^\circ$
 $\mu = 0.397 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
Cut column
 $0.39 \times 0.35 \times 0.35 \text{ mm}$
Amber

$\theta_{\text{max}} = 27.56^\circ$
 $h = -10 \rightarrow 10$
 $k = -22 \rightarrow 0$
 $l = 0 \rightarrow 9$
6 standard reflections every 150 reflections
intensity decay: 10.3% (linear correction)

$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $3.1(1) \times 10^{-6}$
Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Creagh & McAuley (1992) (C, N, O, Cl)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C7	1.315(2)	O3—C2	1.350(2)
O2—C7	1.226(2)		
C7—O1—H1	108(1)	O1—C7—O2	122.2(2)
C2—O3—H2	108(1)	O1—C7—C1	115.2(1)
H1O—O4—H2O	107(2)	O2—C7—C1	122.5(2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

The angles given in brackets following the s.u.'s of each of the best-fit angles are calculated with H atoms fixed at 0.98 \AA from the donor atoms along D—H directions determined by the best fit.

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O4	0.82(2)	1.88(2)	2.681(2)	170(2) [169]
O3—H2...O2	0.95(2)	1.78(2)	2.598(2)	143(2) [142]
O3—H2...Cl1 ⁱ	0.95(2)	2.80(2)	3.367(1)	119(1) [119]
N1—H1N...O4 ⁱⁱ	0.84(2)	2.29(2)	2.995(2)	142(2) [139]
N1—H2N...Cl1 ⁱ	1.04(3)	2.16(3)	3.173(2)	165(2) [166]
N1—H3N...Cl1 ⁱⁱⁱ	0.97(2)	2.15(2)	3.114(2)	175(2) [174]
O4—H1O...Cl1 ^{iv}	0.73(2)	2.70(3)	3.345(2)	149(2) [146]
O4—H2O...Cl1 ^v	0.99(2)	2.18(2)	3.156(2)	170(2) [170]
N1—H1N...O2 ^{vi}	0.84(2)	2.50(2)	2.883(2)	109(2) [106]
N1—H1N...O2 ^{vii}	0.84(2)	2.60(2)	3.147(2)	124(2) [121]
N1—H2N...O2 ^{viii}	1.04(3)	2.57(2)	2.883(2)	97(1) [98]
N1—H3N...O4 ^{ix}	0.97(2)	2.95(2)	2.995(2)	83(1) [83]
O4—H1O...O3 ^x	0.73(2)	2.62(2)	3.025(2)	117(2) [112]
O4—H2O...O3 ^{xi}	0.99(2)	2.88(2)	3.025(2)	89(1) [89]

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

Table 3. First- and basic second-level graph set descriptors involving hydrogen bonds designated a–h in order as given in Table 2

	a	b	c	d	e	f	g	h
a	D	D ₂ ² (6)	D ₂ ² (9)	C ₂ ¹ (9)	D ₂ ² (10)	D ₂ ² (10)	D ₂ ² (4)	D ₂ ² (4)
b		S(6)	D ₂ ¹ (3)	D ₂ ² (10)	D ₂ ² (9)	D ₂ ² (10)	–	–
c			D	D ₂ ² (10)	C ₂ ¹ (9)	C ₂ ¹ (9)	D ₂ ¹ (3)	D ₂ ¹ (3)
d				D	D ₂ ² (5)	D ₂ ² (5)	D ₂ ² (4)	D ₂ ² (4)
e					D	R ₂ ¹ (8)	D ₂ ¹ (3)	D ₂ ¹ (3)
f						D	D ₂ ¹ (3)	D ₂ ¹ (3)
g							D	R ₂ ¹ (8)
h								D

Scan widths were $(1.50 + 0.35 \tan \theta)^\circ$ in ω , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group $P2_1/a$ (No. 14); since refinement proceeded well it was adopted, but subsequently was transformed to the standard setting, $P2_1/c$. Fourier difference methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically. The refined C—H distances range from 0.93 (2) to 0.98 (2) Å, with a mean value of 0.96 (1) Å; refined N—H and O—H distances are given in Table 2. Hydrogen-bond angles were recalculated, with H atoms fixed at 0.98 Å from the donors along the D—H direction determined in the final least-squares fit; these values, in square brackets, are shown in Table 2 after the best-fit values obtained with the refined H atom positions. The maximum effect of extinction is 12.4% of F_o for 012. The maximum positive residual peak is located ~ 1.0 Å from O2; the maximum negative peak is located ~ 1.3 Å from N1.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1127). Services for accessing these data are described at the back of the journal.

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(4R)-(–)-2-Thioxothiazolidine-4-carboxylic Acid (Raphanusamic Acid)

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Abstract

The title acid, C₄H₅NO₂S₂, crystallized in the non-centrosymmetric space group $P2_12_12_1$ with one molecule as the asymmetric unit. Two hydrogen bonds occur, namely, N—H···O, with a donor–acceptor distance of 2.850(2) Å, and O—H···S (resonance induced), with a donor–acceptor distance of 3.318(2) Å; both H atoms involved are ordered. These two types of bonds link a given molecule to four neighbors, the molecules linked being of space-group symmetry types 1 and 3, or 2 and 4. These two subsets of molecules alternate in layers along *c*. Three significant C—H···O interactions occur, one of which crosslinks the subsets just described to produce a three-dimensional network of linked molecules. The absolute structure is determined.

Comment

This report is one of a series on hydrogen bonding in heterocyclic carboxylic acids. It follows reports on 2-aminonicotinic acid and 3-aminopyrazole-4-carboxylic acid (Dobson & Gerkin, 1997, 1998). The title acid, (I), crystallized in the non-centrosymmetric space group $P2_12_12_1$ with a single molecule as the asymmetric unit.