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1-Carboxymethyl-3-hydroxypyridinium chloride–3-hydroxypyridinium-1-acetate (1/1)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.090
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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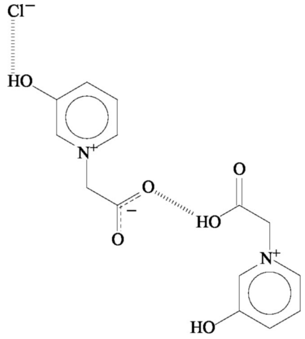
In the crystal structure of the title 1:1 co-crystal, $C_7H_8NO_3^+ \cdot Cl^- \cdot C_7H_7NO_3$, of 1-carboxymethyl-3-hydroxypyridinium chloride with 3-hydroxypyridinium-1-acetate, the cation interacts with the zwitterion to form a ribbon that runs along the c axis of the orthorhombic unit cell. The Cl^- anions lie at the sides of the ribbon.

Comment

Zwitterionic pyridinioacetate (Szafran *et al.*, 1998) is a betaine that affords a plethora of metal carboxylate complexes (Cambridge Structural Database, Version 5.25; Allen, 2002). With a hydroxy substituent at either the 2- or the 4-position of the heterocyclic ring, the resulting compound exists as oxodihydropyridin-1-ylacetic acid (Gao *et al.*, 2004; Rybakov *et al.*, 2002), a neutral compound. The two compounds feature unambiguous single and double bonds in the ring, so that the electrons remain localized in the ring. The 3-hydroxy analogue, on the other hand, should be incapable of such localization, but it could exist in either a zwitterionic or an uncharged configuration. The attempt to ascertain this led to the isolation of 3-hydroxypyridinio-1-acetate as a hemihydrochloride. The compound is formally the title co-crystal of the anticipated betaine with 1-carboxymethyl-3-hydroxypyridinium chloride, *i.e.* $C_7H_8NO_3^+ \cdot Cl^- \cdot C_7H_7NO_3$, (I) (Fig. 1). The *N*-heterocyclic reagent used in the synthesis, 3-hydroxypyridine, is itself aromatic (Ohms *et al.*, 1983), unlike 4-hydroxypyridine, the reagent for the synthesis of the 4-analogue, which is not (Jones, 2001).



(I)

In the co-crystal of (I), the acid entity, *i.e.* the $C_7H_8NO_3^+$ cation, forms a short hydrogen bond through its acid H atom to one of the O atoms of the delocalized carboxyl group ($-CO_2^-$) of the $C_7H_7NO_3$ zwitterion [O5$\cdots$O2 2.519 (2) Å]. The zwitterion uses its hydroxy group to link to the Cl^- anion. Meanwhile, the hydroxy group of the cation interacts with the other carboxyl O atom of the zwitterion to give rise to a ribbon

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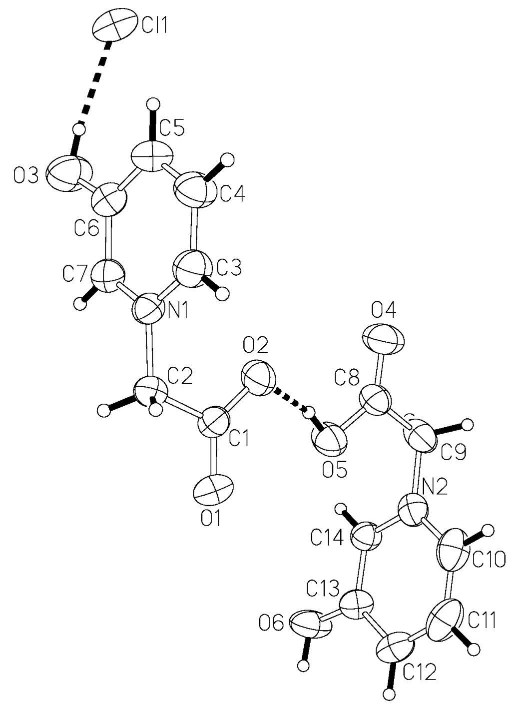

Figure 1
A view of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

motif (Fig. 2). The Cl^- anions are located at the sides of the ribbon.

The hydrogen bond to the Cl^- anion is short, but not extremely short compared with the short bonds found in other systems, *e.g.* pyridinecarboxylic acid hydrochloride [2.041 (1) Å; Nättinen & Rissanen, 2003] and maltol hydrochloride [2.03(4) Å; Bilodeau & Beauchamp, 1996].

Experimental

An aqueous solution of 3-hydroxypyridine (9.55 g, 0.10 mol) and sodium hydroxide (4.00 g, 0.10 mol) was reacted with an aqueous solution of chloroacetic acid (14.18 g, 0.10 mol) that had been neutralized with sodium hydroxide (6.00 g, 0.15 mol). The pH of the mixture was approximately 9–10. The mixture was refluxed for 5 h. The cooled solution was then treated with 0.05 *M* hydrochloric acid to a pH of 2–3. The solution was then filtered. Colourless crystals of (I) were obtained after several days. Analysis, calculated for $C_{14}H_{15}ClN_2O_6$: C 49.06, H 4.41, N 8.17%; found: C 49.14, H 4.49, N 8.21%.

Crystal data

$C_7H_8NO_3^+\cdot Cl^-\cdot C_7H_7NO_3$
$M_r = 342.73$
Orthorhombic, $Pca2_1$
$a = 30.983$ (6) Å
$b = 4.920$ (1) Å
$c = 9.981$ (2) Å
$V = 1521.4$ (5) Å^3
$Z = 4$
$D_x = 1.496$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 151 reflections
$\theta = 3.3$–27.4°
$\mu = 0.29$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.42 × 0.35 × 0.26 mm

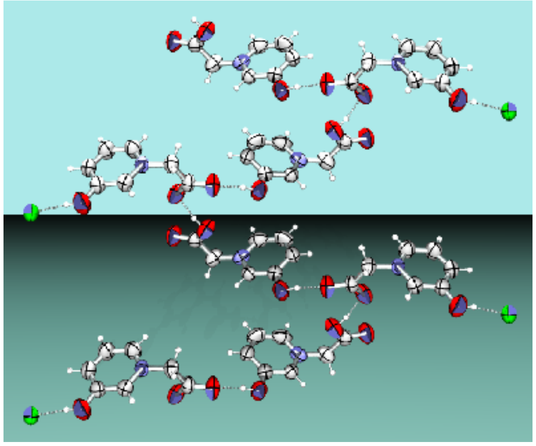

Figure 2
A plot of the hydrogen-bonded (dashed lines) chain structure of (I), viewed along the *c* axis.

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.709$, $T_{max} = 0.930$
13 459 measured reflections
3484 independent reflections
3315 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$
$h = -39 \rightarrow 40$
$k = -6 \rightarrow 6$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.01$
3484 reflections
220 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 0.1351P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Absolute structure: Flack (1983), with 1637 Friedel pairs
Flack parameter = −0.01 (5)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.252 (2)	N2—C14	1.343 (2)
O2—C1	1.252 (2)	C1—C2	1.522 (2)
O3—C6	1.339 (2)	C3—C4	1.382 (2)
O4—C8	1.202 (2)	C4—C5	1.383 (3)
O5—C8	1.297 (2)	C5—C6	1.388 (2)
O6—C13	1.337 (2)	C6—C7	1.394 (2)
N1—C2	1.479 (2)	C8—C9	1.519 (2)
N1—C3	1.338 (2)	C10—C11	1.373 (3)
N1—C7	1.341 (2)	C11—C12	1.373 (3)
N2—C9	1.476 (2)	C12—C13	1.392 (2)
N2—C10	1.346 (2)	C13—C14	1.388 (2)
C2—N1—C3	118.8 (1)	O3—C6—C7	117.2 (2)
C2—N1—C7	119.2 (1)	C5—C6—C7	118.5 (2)
C3—N1—C7	122.0 (1)	N1—C7—C6	120.4 (1)
C9—N2—C10	119.9 (2)	O4—C8—O5	126.3 (2)
C9—N2—C14	119.1 (1)	O4—C8—C9	119.5 (2)
C10—N2—C14	121.0 (2)	O5—C8—C9	114.2 (1)
O1—C1—O2	127.0 (2)	N2—C9—C8	113.8 (1)
O1—C1—C2	114.7 (1)	N2—C10—C11	120.0 (2)
O2—C1—C2	118.3 (1)	C10—C11—C12	120.7 (2)
N1—C2—C1	112.6 (1)	C11—C12—C13	118.8 (2)
N1—C3—C4	119.8 (2)	O6—C13—C12	124.6 (2)
C3—C4—C5	119.8 (2)	O6—C13—C14	116.5 (1)
C4—C5—C6	119.6 (2)	C12—C13—C14	118.9 (2)
O3—C6—C5	124.3 (2)	N2—C14—C13	120.6 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···Cl1	0.85 (1)	2.15 (1)	2.990 (2)	171 (3)
O5—H5O···O2	0.86 (1)	1.68 (1)	2.519 (2)	165 (3)
O6—H6O···O1^{i}	0.86 (1)	1.72 (1)	2.570 (2)	169 (3)

Symmetry code: (i) $\frac{3}{2} - x, y, z - \frac{1}{2}$.

The acid and hydroxy H atoms were located and refined isotropically, with O—H and H···H distances restrained to 0.85 (1) and 1.39 (1) Å, respectively. All other H atoms were placed in calculated positions, with aromatic C—H = 0.93 and aliphatic C—H = 0.97 Å, and were included in the refinement in the riding-model approximation, with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$.

Data collection: *RAPID AUTO* (Rigaku, 1998); cell refinement: *RAPID AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *POV-Ray* (Cason, 2002); software used to prepare material for publication: *SHELXL*97.

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