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4-Carboxypyridinium hydrogen chloranilate monohydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.092
Data-to-parameter ratio = 13.8

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

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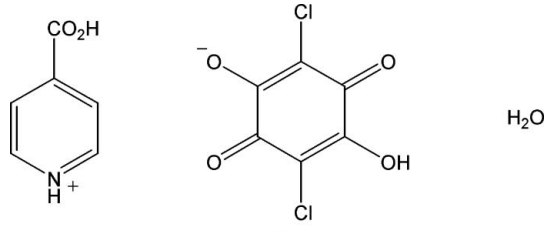
The title compound (systematic name: 4-carboxypyridinium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate monohydrate), $C_6H_6NO_2^+\cdot C_6HCl_2O_4^-\cdot H_2O$, is a monohydrate salt of chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) with isonicotinic acid (pyridine-4-carboxylic acid), in which an acid–base interaction involving a proton transfer is observed from the chloranilic acid to the pyridine group of isonicotinic acid. In the crystal structure, the 4-carboxypyridinium cation, the hydrogen chloranilate anion and the water molecule are held together through N—H···O, O—H···O and C—H···O hydrogen bonds, forming a chain. The chains are further linked by O—H···O and C—H···O hydrogen bonds, forming a three-dimensional hydrogen-bond network.

Comment

The title compound, (I), was prepared in order to extend our study on *D*—H···*A* hydrogen bonding (*D* = N, O, or C; *A* = N, O or Cl) in chloranilic acid–amine 1:1 and 1:2 systems (Tabuchi *et al.*, 2005). Chloranilic acid is attractive as a template for generating tightly bound self-assemblies with polarizable bases, as well as a model compound for investigating proton-transfer motions in intermolecular hydrogen bonds by ^{1}H NMR and ^{35}Cl NQR techniques (Ikeda *et al.*, 2005).



(I)

The asymmetric unit in the title compound, (I), contains a 4-carboxypyridinium cation, a hydrogen chloranilate anion and a water molecule; an acid–base interaction involving a proton transfer is observed between the chloranilic acid and the isonicotinic acid through the water molecule and these three molecules are held together by N1—H2···O7, O7—H8···O4 and C11—H6···O1 hydrogen bonds (Fig. 1 and Table 1). The three components are further connected by three O—H···O hydrogen bonds [O2—H1···O7^{i}, O5—H7···O3^{ii} and O7—H9···O6^{iii}; symmetry codes (i)–(iii) are given in Table 2], resulting in a hydrogen-bonded chain running along the [1$\bar{1}$0] direction (Fig. 2). Atom H1 is also involved in an intramolecular hydrogen bond with O3. Neighboring chains related

by an *n*-glide plane to each other are linked through the water molecule, forming a three-dimensional hydrogen-bond network. Besides the O—H···O hydrogen bonds, there are C—H···O hydrogen bonds between the chains.

Experimental

Crystals were obtained by slow evaporation of an ethanol solution of chloranilic acid with isonicotinic acid in a 1:1 molar ratio (0.200 and 0.118 g for chloranilic acid and isonicotinic acid, respectively).

Crystal data

$C_6H_6NO_2^+\cdot C_6HCl_2O_4^-\cdot H_2O$
M_r = 350.11
Monoclinic, $P2_1/n$
a = 12.9472 (3) Å
b = 7.7206 (2) Å
c = 13.8128 (3) Å
β = 93.4766 (11)°
V = 1378.19 (6) Å^3
Z = 4
D_x = 1.687 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.51 mm^{-1}
T = 298 K
Prism, brown
0.50 × 0.40 × 0.30 mm

Data collection

Rigaku R-AXIS-IV diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.779, T_{max} = 0.859
10144 measured reflections
3041 independent reflections
2728 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.092
S = 1.08
3041 reflections
220 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.6445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···O7	0.89 (3)	1.90 (2)	2.7286 (19)	154 (2)
O2—H1···O3	0.84 (3)	2.10 (3)	2.6073 (16)	119 (2)
O2—H1···O7^{i}	0.84 (3)	2.08 (3)	2.8175 (17)	146 (2)
O5—H7···O3^{ii}	0.89 (3)	1.68 (3)	2.5633 (17)	175 (3)
O7—H8···O4	0.80 (3)	1.97 (3)	2.7542 (18)	166 (3)
O7—H9···O6^{iii}	0.88 (3)	2.02 (3)	2.8799 (18)	165 (3)
C7—H3···O4^{iv}	0.93	2.31	3.168 (2)	153
C10—H5···O2^{v}	0.93	2.40	3.3063 (19)	164
C11—H6···O1	0.93	2.36	2.9989 (19)	126

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

H atoms attached to O and N atoms were found in a difference Fourier map and refined isotropically (refined distances given in Table 1). Other H atoms were treated as riding, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

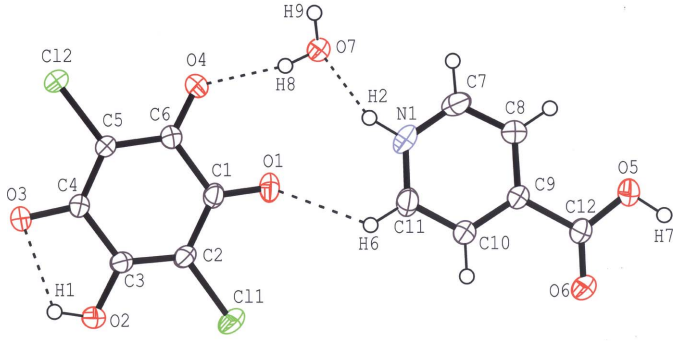


Figure 1
The asymmetric unit of (I), with the atom numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O, O—H···O and C—H···O hydrogen bonds are indicated by dashed lines.

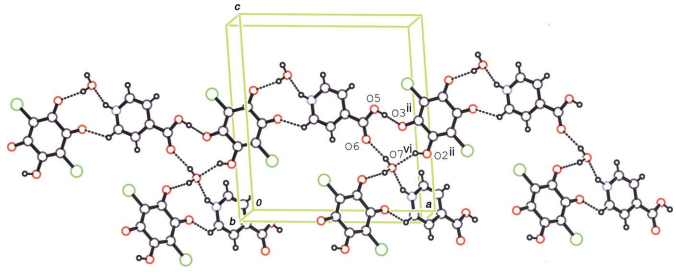


Figure 2
A partial packing diagram, viewed approximately along the *b* axis, showing the hydrogen-bonded chain and hydrogen-bonding scheme around the water molecule. Dashed lines show N—H···O, O—H···O and C—H···O hydrogen bonds [symmetry codes: (ii) $1+x, y-1, z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$].

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