

2-Carboxypyridinium hydrogen chloranilate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.031
wR factor = 0.072
Data-to-parameter ratio = 12.8

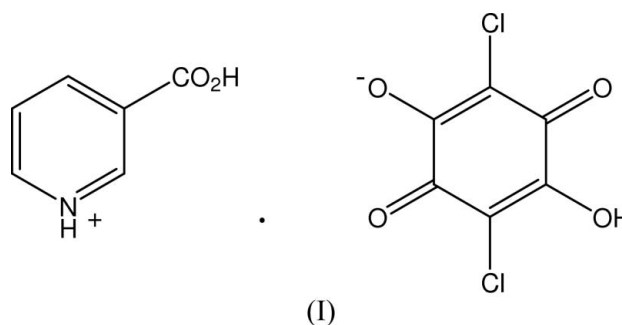
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{C}_6\text{HCl}_2\text{O}_4^-$, is the salt of chloranilic acid with nicotinic acid (2-carboxypyridine), where an acid–base interaction involving a proton transfer is observed from the chloranilic acid to the pyridine group of nicotinic acid. In the crystal structure, the hydrogen chloranilate anion and the 2-carboxypyridinium cation are linked by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to form a zigzag chain. The chains are further linked by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to form a three-dimensional hydrogen-bond network.

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Comment

The title compound, (I), was prepared in order to extend our study on $D-\text{H} \cdots A$ hydrogen bonding ($D = \text{N}, \text{O}$ or C ; $A = \text{N}, \text{O}$ or Cl) in chloranilic acid–amine 1:1 and 1:2 systems (Fukunaga & Ishida, 2003; Fukunaga *et al.*, 2003; Ishida, 2004*a,b,c,d,e*). Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) is a strong dibasic acid endowed with hydrogen-bond donor and acceptor groups, and appears particularly attractive as a template for generating tightly bound self-assemblies with polarizable bases (Ishida & Kashino, 1999*a,b,c*, 2000, 2001, 2002; Zaman *et al.*, 1999, 2000), as well as a model compound for investigating proton-transfer motions in intermolecular hydrogen bonds by ^1H NMR and ^{35}Cl NQR techniques (Nihei *et al.*, 2000*a,b*; Ikeda *et al.*, 2005).



In (I), the asymmetric unit is composed of $\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{C}_6\text{HCl}_2\text{O}_4^-$; an acid–base interaction involving a proton transfer is observed between chloranilic acid and nicotinic acid (Fig. 1). The cations and anions are stacked in columns along the b axis. The two components are linked by a bifurcated hydrogen bond ($\text{N1}-\text{H2} \cdots \text{O1}$ and $\text{N1}-\text{H2} \cdots \text{O4}$) and an $\text{O2}-\text{H1} \cdots \text{O6}^i$ hydrogen bond (Table 2) to form a zigzag chain running along the $[1\bar{1}1]$ direction. Atom H1 is also involved in an intramolecular hydrogen bond with O3. The dihedral angle between the C1–C6 plane of the anion and the pyridinium ring is $84.18(15)^\circ$. Neighboring chains related

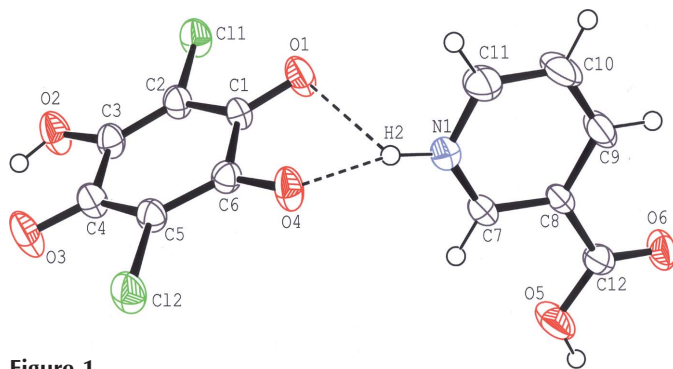


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I), with the atom numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H...O hydrogen bonds are indicated by dashed lines.

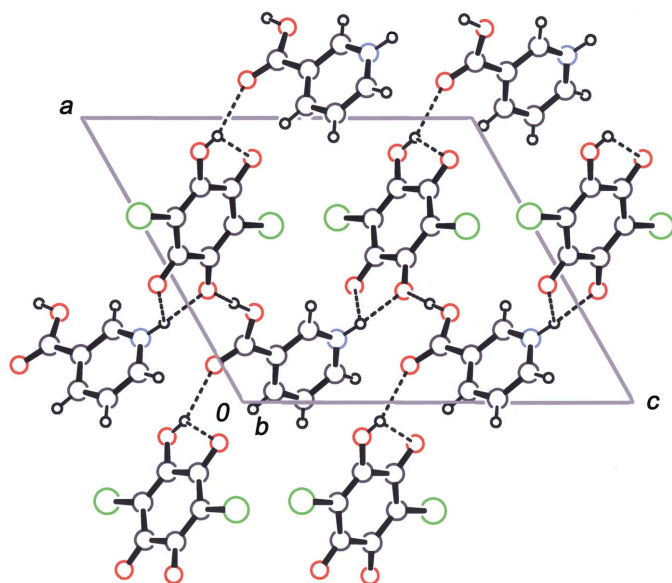


Figure 2
Packing diagram, viewed down the *b* axis. Dashed lines show N—H...O and O—H...O hydrogen bonds.

to each other by a *c*-glide plane are connected by an O5—H7...O4ⁱⁱ hydrogen bond (Table 2) to form a three-dimensional hydrogen-bond network (Fig. 2). Besides the O—H...O and N—H...O hydrogen bonds, there are C—H...O hydrogen bonds between neighboring chains (Table 2).

Experimental

Crystals were obtained by slow evaporation from a methanol solution of chloranilic acid with nicotinic acid in a 1:1 molar ratio.

Crystal data

C₆H₆NO₂⁺·C₆HCl₂O₄⁻
M_r = 332.10
 Monoclinic, *Pc*
a = 10.7715 (10) Å
b = 5.4301 (5) Å
c = 12.9139 (12) Å
 β = 119.580 (7)°
V = 656.89 (11) Å³
Z = 2

D_x = 1.679 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2638 reflections
 θ = 4.2–27.4°
 μ = 0.52 mm⁻¹
T = 295 K
 Prism, brown
 0.25 × 0.25 × 0.20 mm

Data collection

Rigaku R-Axis IV diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.835, *T_{max}* = 0.901
 4509 measured reflections
 2602 independent reflections

2312 reflections with *I* > 2σ(*I*)
R_{int} = 0.021
 θ_{max} = 27.5°
h = -13 → 13
k = -6 → 6
l = -16 → 16

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.031
wR(*F*²) = 0.072
S = 1.01
 2602 reflections
 204 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.0699P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 0.21 e Å⁻³
 Δρ_{min} = -0.19 e Å⁻³
 Absolute structure: Flack (1983),
 1100 Friedel pairs
 Flack parameter: 0.54 (6)

Table 1

Selected bond lengths (Å).

C1—C2	1.729 (3)	O4—C6	1.277 (3)
C12—C5	1.740 (3)	O5—C12	1.308 (3)
O1—C1	1.217 (3)	O6—C12	1.211 (3)
O2—C3	1.337 (3)	C1—C6	1.544 (4)
O3—C4	1.227 (4)	C3—C4	1.504 (4)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H1...O3	0.84 (4)	2.09 (4)	2.598 (3)	118 (4)
O2—H1...O6 ⁱ	0.84 (4)	2.11 (5)	2.847 (3)	146 (4)
O5—H7...O4 ⁱⁱ	1.00 (5)	1.59 (5)	2.576 (3)	169 (5)
N1—H2...O1	0.96 (4)	2.39 (4)	2.921 (3)	114 (3)
N1—H2...O4	0.96 (4)	1.81 (4)	2.743 (3)	164 (3)
C7—H3...O1 ⁱⁱⁱ	0.93	2.36	3.080 (3)	134
C9—H4...O3 ^{iv}	0.93	2.45	3.037 (3)	121
C10—H5...C11 ^v	0.93	2.81	3.728 (4)	168
C11—H6...O2 ^v	0.93	2.55	3.232 (4)	131

Symmetry codes: (i) *x* + 1, *y* - 1, *z* + 1; (ii) *x*, -*y* + 1, *z* - ½; (iii) *x*, *y* + 1, *z*; (iv) *x* - 1, *y*, *z* - 1; (v) *x* - 1, -*y* - 1, *z* - ½.

H atoms attached to O and N atoms were found in a difference Fourier map and refined isotropically (refined distances given in Table 2). Other H atoms were treated as riding, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The value of the Flack (1983) parameter indicates that the crystal is an inversion twin with almost equal contributions of the two components.

Data collection: *PROCESS-AUTO* (Rigaku/MSC & Rigaku Corporation, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 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).

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