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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.033
 wR factor = 0.083
Data-to-parameter ratio = 11.6

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

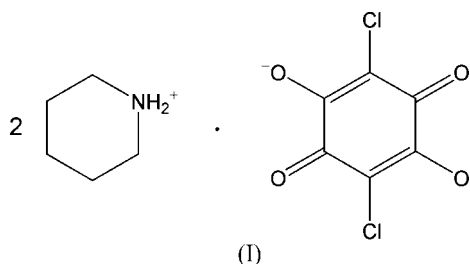
Bis(piperidinium) chloranilate

In the title crystal structure, $2\text{C}_5\text{H}_{12}\text{N}^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}$, chloranilate and piperidinium ions are connected by bifurcated $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, giving a centrosymmetric chloranilate–piperidinium 1:2 unit. The 1:2 units are connected to each other by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a molecular ladder. There is a centre of symmetry at the centre of the anion ring.

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Comment

Crystal structures in the chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone)–secondary amine system have been analyzed for 1:1 salts of morpholine (Ishida & Kashino, 1999), diethylamine (Ishida & Kashino, 2000), piperidine (Fukunaga & Ishida, 2003) and 1,2,3,4-tetrahydroquinoline (Ishida, 2004*b*), and for a 1:2 salt of pyrrolidine (Ishida, 2004*a*). In the present study, we have prepared the 1:2 salt (I) and determined its crystal structure at 100 K in order to extend the previous studies.



In the crystal structure of (I), the asymmetric unit is composed of $\text{C}_5\text{H}_{12}\text{N}^+\cdot 0.5\text{C}_6\text{O}_4\text{Cl}_2^{2-}$, and an acid–base interaction involving proton transfer is observed between chloranilic acid and piperidine (Fig. 1). There is a centre of symmetry at the centre of the anion ring. The chloranilate and piperidinium ions are connected by asymmetric bifurcated

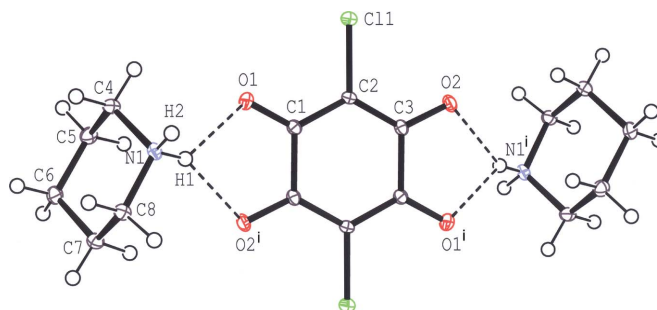


Figure 1
View of (I), with the atom labelling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are indicated by dashed lines (the symmetry code is as in Table 1).

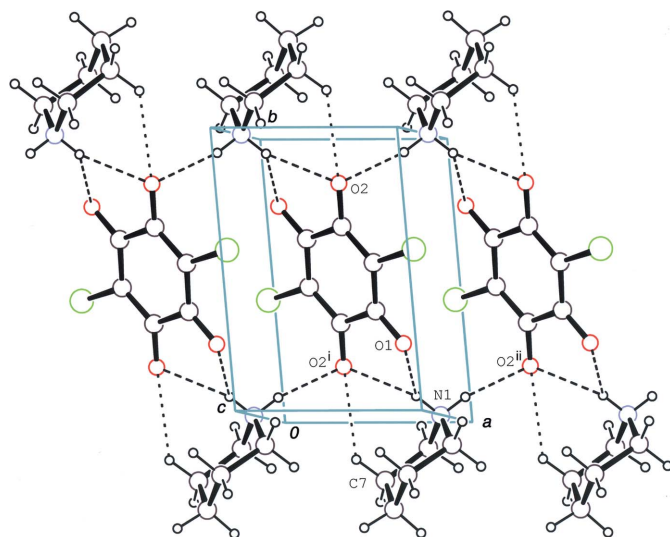


Figure 2

Packing view of (I), showing a ladder along the *a* axis. N—H...O and C—H...O hydrogen bonds are indicated by dashed and dotted lines, respectively (the symmetry codes are as in Table 2).

N—H...O hydrogen bonds (Table 2) to give a centrosymmetric chloranilate-piperidinium 1:2 unit. Within the unit, there is also a weak C—H...O hydrogen bond. The 1:2 units are connected by other N—H...O hydrogen bonds, forming a ladder running parallel to the *a* axis. The packing scheme is similar to that found in bis(pyrazolium) chloranilate (Ishida & Kashino, 2001) and bis(3-methylpyrazolium) chloranilate (Ishida, 2004c), but quite different from that in bis(pyrrolidinium) chloranilate (Ishida, 2004a), where the two cations and one anion are arranged in an alternating manner to form a tape.

Experimental

To a solution of piperidine (85 mg, 1 mmol) in CH₃OH (10 ml), a solution of chloranilic acid (209 mg, 1 mmol) in CH₃OH (25 ml) was added at room temperature. The solution was allowed to evaporate slowly at room temperature. Dark-red crystals of (I) suitable for X-ray diffraction were formed, filtered off and dried under vacuum.

Crystal data

2C ₅ H ₁₂ N ⁺ ·C ₆ Cl ₂ O ₄ ²⁻	<i>V</i> = 418.25 (5) Å ³
<i>M_r</i> = 379.28	<i>Z</i> = 1
Triclinic, <i>P</i> 1	<i>D_x</i> = 1.506 Mg m ⁻³
<i>a</i> = 5.1239 (3) Å	Mo <i>K</i> α radiation
<i>b</i> = 8.7058 (7) Å	<i>μ</i> = 0.41 mm ⁻¹
<i>c</i> = 10.4508 (7) Å	<i>T</i> = 100 (2) K
<i>α</i> = 114.412 (3)°	Prism, dark red
<i>β</i> = 95.561 (2)°	0.28 × 0.15 × 0.08 mm
<i>γ</i> = 95.070 (3)°	

Data collection

Rigaku R-AXIS RAPID II diffractometer	4040 measured reflections
<i>ω</i> scans	1838 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1534 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.781, <i>T_{max}</i> = 0.968	<i>R_{int}</i> = 0.045
	<i>θ_{max}</i> = 27.1°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.033
wR (*F*²) = 0.083
S = 1.08
 1838 reflections
 158 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.1379P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.38 e Å⁻³
 Δρ_{min} = -0.38 e Å⁻³

Table 1

Selected bond lengths (Å).

C1—C2	1.7466 (16)	N1—C8	1.494 (2)
O1—C1	1.2372 (19)	C1—C2	1.423 (2)
O2—C3	1.2662 (18)	C1—C3 ⁱ	1.545 (2)
N1—C4	1.493 (2)	C2—C3	1.389 (2)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

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>
N1—H1...O1	0.88 (2)	2.13 (2)	2.8045 (19)	133.1 (17)
N1—H1...O2 ⁱ	0.88 (2)	2.20 (2)	2.9929 (19)	150.7 (17)
N1—H2...O2 ⁱⁱ	0.86 (2)	1.98 (2)	2.8070 (19)	162 (2)
C7—H9...O2 ⁱ	0.99 (2)	2.59 (2)	3.349 (2)	133.5 (17)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.

H atoms were located in a Fourier map and refined isotropically; N—H and C—H bond lengths are in the range 0.86 (2)–0.88 (2) Å and 0.95 (2)–1.01 (2) Å, respectively.

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*.

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