Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Cytosinium hydrogen chloranilate monohydrate

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Received 19 September 2006
Accepted 22 September 2006

The title compound, $C_4H_6N_3O^+\cdot C_6HCl_2O_4^-\cdot H_2O$, is a monohydrate salt of chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) with cytosine [4-aminopyrimidine-2(1*H*)-one]. In the crystal structure, the cytosinium cation, the hydrogen chloranilate anion and the water molecule are held together through O—H···O, N—H···O, N—H···Cl and C—H···O hydrogen bonds, forming a molecular tape. The tapes are further linked by O—H···Cl and C—H···Cl hydrogen bonds, forming a three-dimensional hydrogen-bond network.

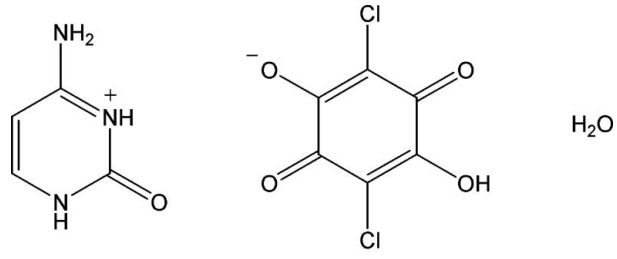
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.073
Data-to-parameter ratio = 15.9

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

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 the chloranilic acid–pyridine system. Crystal structures have been analyzed for the compounds of diazine (Ishida & Kashino, 1999*a*,*b*,*c*), methylpyridine (Ishida & Kashino, 2002; Ishida, 2004*a*,*b*) and carboxypyridine (Tabuchi *et al.*, 2005; Gotoh *et al.*, 2006). Cytosine, one of the nucleotide building blocks, is a strong base and forms salts with organic acids. As such, several crystal structures have been reported (Tamura *et al.*, 1972; Ohki *et al.*, 1975; Takenaka *et al.*, 1980; Gdaniec *et al.*, 1988, 1989; Balasubramanian *et al.*, 1996; Smith *et al.*, 2005).



(I)

The asymmetric unit in (I) contains a cytosinium cation, a hydrogen chloranilate anion and a water molecule. The three components are held together by bifurcated N—H···O (N1—H2···O1 and N1—H2···O4) and O—H···O (O6—H8···O4 and O6—H8···O5) hydrogen bonds, and a C10—H7···O1 hydrogen bond (Fig. 1 and Table 1). Atom H1 participates only in an intramolecular hydrogen bond (O2—H1···O3). The neighboring units related by an inversion center are connected by N2—H3···O5^{i} and N3—H4···O6^{i} hydrogen bonds (symmetry codes as in Table 1), resulting in a centrosymmetric dimeric unit (Fig. 2). The dimeric units are further connected by N3—H5···O3^{ii} and N3—H5···Cl2^{ii} hydrogen bonds (Table 1), forming a molecular tape running along the

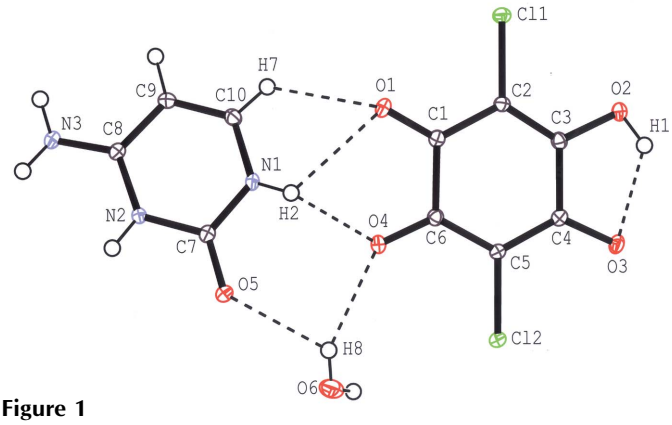


Figure 1
The asymmetric unit of (I), with the atom numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O, O—H···O and C—H···O hydrogen bonds are indicated by dashed lines.

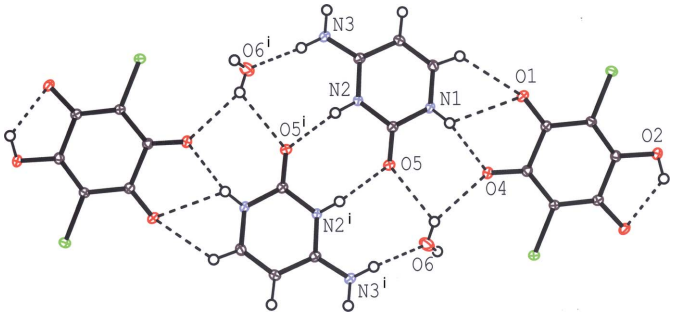


Figure 2
A view of the dimeric unit of (I), showing the hydrogen-bonding scheme (dashed lines) [symmetry code (i) as given in Table 1].

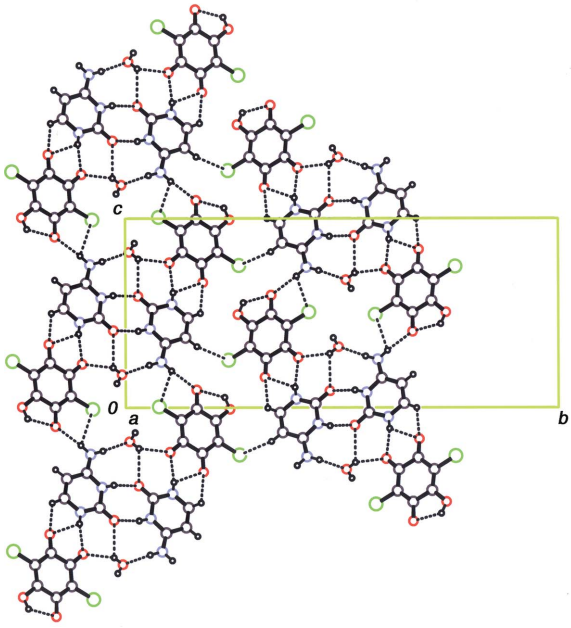


Figure 3
A partial packing diagram, viewed down the *a* axis, showing the hydrogen-bonded tape and the hydrogen-bonding scheme. Dashed lines show N—H···O, O—H···O, C—H···O, N—H···Cl and C—H···Cl hydrogen bonds.

[10$\bar{1}$] direction. The tapes are stacked along the *a* axis through O6—H9···Cl2^{iii} hydrogen bonds. The neighboring tapes related by an *n*-glide plane to each other are linked weakly through C9—H6···Cl1^{iv} hydrogen bonds (Fig. 3).

Experimental

Crystals were obtained by slow evaporation of a methanol solution (50 ml) of chloranilic acid with cytosine in a 1:1 molar ratio (0.062 and 0.033 g for chloranilic acid and cytosine, respectively).

Crystal data

$C_4H_6N_3O^+\cdot C_6HCl_2O_4^-\cdot H_2O$
M_r = 338.10
Monoclinic, $P2_1/n$
a = 3.6656 (1) Å
b = 27.8941 (15) Å
c = 12.1499 (5) Å
β = 92.3075 (15)°
V = 1241.30 (9) Å^3
Z = 4
D_x = 1.809 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.56 mm^{-1}
T = 100 (2) K
Needle, black
0.30 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.791, T_{max} = 0.946
14606 measured reflections
3612 independent reflections
3126 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 30.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.073
S = 1.05
3612 reflections
227 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.179P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···O1	0.796 (17)	2.475 (17)	2.9707 (13)	121.6 (15)
N1—H2···O4	0.796 (17)	1.997 (17)	2.7748 (12)	165.6 (17)
N2—H3···O5^{i}	0.826 (17)	2.002 (17)	2.7973 (14)	161.4 (16)
N3—H4···O6^{i}	0.849 (19)	1.911 (19)	2.7579 (16)	175.6 (18)
N3—H5···O3^{ii}	0.861 (16)	2.038 (16)	2.8964 (13)	174.7 (16)
N3—H5···Cl2^{ii}	0.861 (16)	2.830 (16)	3.2278 (10)	110.1 (12)
O2—H1···O3	0.83 (2)	2.03 (2)	2.6084 (12)	126.6 (19)
O6—H8···O4	0.77 (3)	2.32 (3)	3.0171 (15)	151 (2)
O6—H8···O5	0.77 (3)	2.39 (2)	2.8942 (14)	124 (2)
O6—H9···Cl2^{iii}	0.78 (3)	2.68 (3)	3.4497 (13)	169 (2)
C9—H6···Cl1^{iv}	0.945 (16)	2.794 (16)	3.5494 (12)	137.6 (11)
C10—H7···O1	0.921 (16)	2.438 (14)	3.0362 (13)	122.7 (12)

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

H atoms were refined without constraints.

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).

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 16550014) from the Japan Society for the Promotion of Science.

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