Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(3-picolinium) chloranilate dihydrate

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Key indicators

Single-crystal X-ray study
T = 301 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.104
Data-to-parameter ratio = 16.6

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

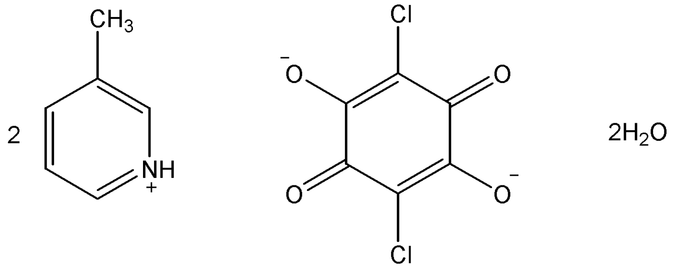
In the title compound, $2\,C_6H_8N^+\cdot C_6Cl_2O_4^{2-}\cdot 2H_2O$, the chloranilate and 3-picolinium (3-methylpyridinium) ions are connected by N—H···O hydrogen bonds to give a centrosymmetric chloranilate–3-picolinium 1:2 unit. The structure consists of layers of the 1:2 units, and water molecules link the layers through O—H···O and C—H···O hydrogen bonds.

Received 15 September 2004
Accepted 20 September 2004
Online 30 September 2004

Comment

The title compound, (I), was prepared in order to extend our study of *D*—H···*A* hydrogen bonding (*D* = N, O and C; *A* = N, O and Cl) in the chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone)–amine 1:2 system. Crystal structures have been analyzed for the 1:2 complexes of pyridazine, pyrimidine, pyrazine (Ishida & Kashino, 1999*a*,*b*), pyrazole, imidazole (Ishida & Kashino, 2001), toluidine (Fukunaga *et al.*, 2003) and pyrrolidine (Ishida, 2004).

In (I), the chloranilate and 3-picolinium ions are held together by bifurcated N—H···O hydrogen bonds (Table 2) to give a chloranilate–3-picolinium 1:2 unit, which is located on an inversion center, similar to that observed in diazine complexes (Fig. 1). The planes of the chloranilate ring and the pyridine ring are almost coplanar, the angle between them being 9.5 (1)°. The 1:2 units are stacked through π–π interactions between the pyridine rings, resulting in a layer parallel to (001) (Fig. 2). The closest separation between the pyridine rings in the layer is 3.497 (3) Å, and the center-to-center separation is 3.863 (3) Å. The water molecules link neighboring layers through O—H···O and C—H···O hydrogen bonds (Table 2) to form a three-dimensional hydrogen-bond network.



(I)

Experimental

Crystals were obtained by slow evaporation of an acetonitrile solution of chloranilic acid and 3-picoline in a 1:2 molar ratio.

doi: 10.1107/S1600536804023256

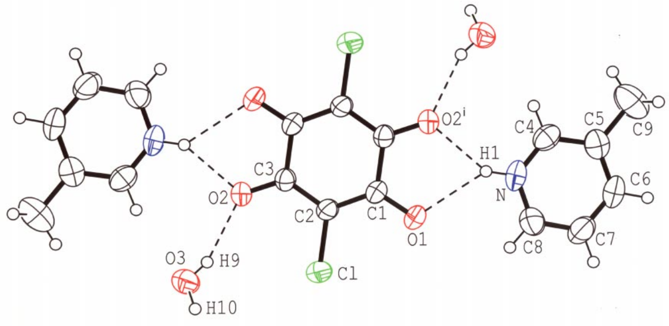


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I), showing the atom labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O and O—H···O hydrogen bonds are indicated by dashed lines (the symmetry code is as in Table 1).

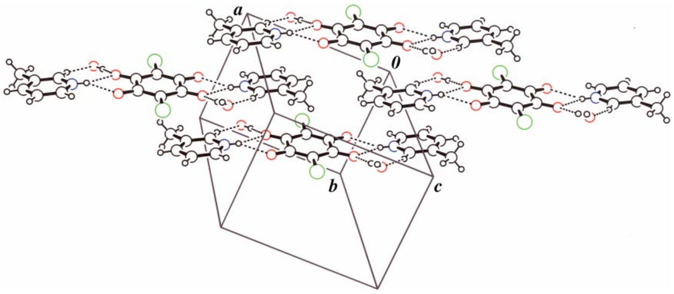


Figure 2
Packing diagram of (I), showing a molecular layer formed by π–π stacking interactions.

Crystal data

$2C_6H_8N^+\cdot C_6Cl_2O_4^{2-}\cdot 2H_2O$
$M_r = 431.27$
Monoclinic, $P2_1/c$
$a = 9.212$ (6) Å
$b = 7.349$ (2) Å
$c = 15.045$ (4) Å
$\beta = 98.52$ (3)°
$V = 1007.4$ (8) Å^3
$Z = 2$
$D_x = 1.422$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.6$–$12.0°$
$\mu = 0.36$ mm^{-1}
$T = 301$ K
Prism, purple
0.40 × 0.30 × 0.15 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.879$, $T_{\max} = 0.948$
3034 measured reflections
2320 independent reflections
1521 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 27.5°$
$h = -2 \rightarrow 11$
$k = 0 \rightarrow 9$
$l = -19 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
$S = 1.00$
2320 reflections
140 parameters
H atoms treated by a mixture of constrained and independent refinement
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.191P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Cl—C2	1.7339 (19)	C1—C2	1.398 (3)
O1—C1	1.244 (2)	C1—C3^i	1.540 (3)
O2—C3	1.249 (2)	C2—C3	1.392 (3)
N—C8	1.324 (3)	C5—C9	1.499 (3)
N—C4	1.332 (3)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1···O1	0.82 (3)	2.26 (3)	2.917 (3)	137 (3)
N—H1···O2^i	0.82 (3)	2.04 (3)	2.755 (3)	147 (3)
O3—H9···O2	0.78 (3)	2.09 (3)	2.826 (3)	158 (3)
O3—H10···O1^{ii}	0.89 (3)	2.02 (3)	2.859 (3)	158 (3)
C4—H2···O3^i	0.93	2.39	3.295 (4)	164
C8—H5···O3^{iii}	0.93	2.39	3.243 (4)	152

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

H atoms attached to N and O atoms were refined isotropically. Methyl H atoms were positioned geometrically (C—H = 0.96 Å) and refined as riding, with free rotation about the C—C bond. $U_{\rm iso}$(H) values were set at $1.5U_{\rm eq}$(C). Aromatic H atoms were also treated as riding, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

X-ray measurements were made at the X-Ray Laboratory of Okayama University. This work was supported by the Mitsubishi Foundation.

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