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Bis(2,4,6-trimethylpyridinium) chloranilate

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In the title compound, $2C_8H_{12}N^+\cdot C_6Cl_2O_4{}^{2-}$, the cation and the anion are held together by bifurcated N—H···O hydrogen bonds to give a centrosymmetric chloranilate–trimethylpyridinium 1:2 unit. The 1:2 units are connected by C—H···O hydrogen bonds to form a molecular layer.

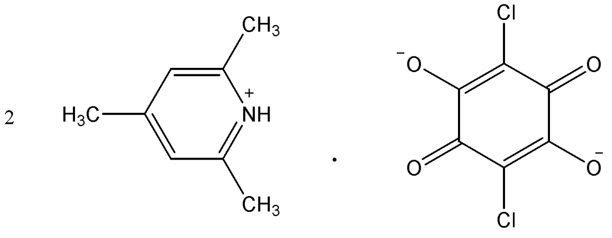
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.122
Data-to-parameter ratio = 18.3

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 of D—H···A hydrogen bonding (D = N, O or C; A = N, O or Cl) in the chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone)–amine 1:2 system. Crystal structures have been analyzed for 1:2 complexes of diazine (Ishida & Kashino, 1999*a*,*b*), diazole (Ishida & Kashino, 2001), toluidine (Fukunaga *et al.*, 2003), pyrrolidine (Ishida, 2004*a*) and picoline (Ishida, 2004*b*). Proton-transfer motions in the intermolecular hydrogen bonds have been observed for the 1:2 complexes of pyridazine and pyrazine by ^{1}H NMR and ^{35}Cl NQR techniques (Nihei *et al.*, 2000*a*,*b*).



(I)

In (I), the asymmetric unit is composed of one 2,4,6-trimethylpyridinium cation and half a chloranilate anion. The ions are held together by bifurcated N—H···O hydrogen bonds (Table 2) to give a centrosymmetric chloranilate–trimethylpyridinium 1:2 unit, similar to that observed in the diazine complexes (Fig. 1). The chloranilate ion shows a

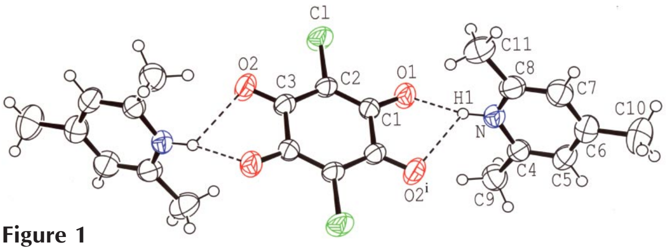


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O hydrogen bonds are indicated by dashed lines. Unlabeled atoms are related to labeled atoms by $2 - x$, $2 - y$, $1 - z$. [Symmetry code (i) is as in Table 1.]

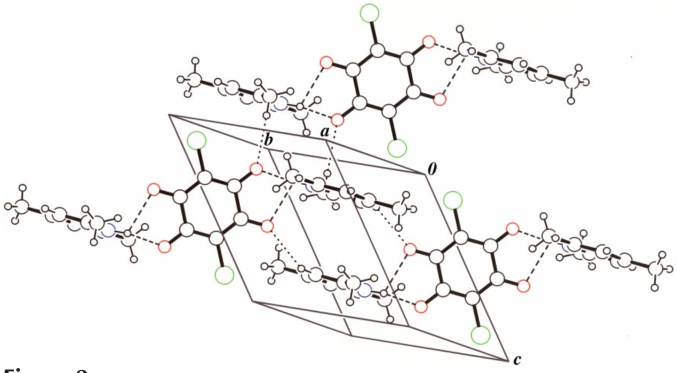


Figure 2
Packing diagram of (I), showing a molecular layer formed by N—H···O and C—H···O hydrogen bonds, which are indicated by dashed and dotted lines, respectively.

characteristic structure, having four short C—C bonds and two extremely long C—C bonds (Table 1), which is explainable in terms of the double π system of the anion (Andersen, 1967; Benchekroun & Savariault, 1995). The planes of the chloranilate ring and the pyridine ring are almost perpendicular, the angle between them being 80.04 (4)°, probably due to the steric repulsion between the methyl groups and the O atoms of the anion. The 1:2 units are connected by C—H···O hydrogen bonds (Table 2) to form a molecular layer extending parallel to the (110) plane (Fig. 2).

Experimental

Crystals were obtained by slow evaporation of an acetonitrile solution of chloranilic acid and 2,4,6-trimethylpyridine in a 1:2 molar ratio.

Crystal data

$2C_8H_{12}N^+\cdot C_6Cl_2O_4^{2-}$
$M_r = 451.35$
Triclinic, $P\overline{1}$
$a = 8.4902$ (9) Å
$b = 9.0205$ (16) Å
$c = 9.3236$ (14) Å
$\alpha = 115.456$ (12)°
$\beta = 112.034$ (10)°
$\gamma = 94.799$ (13)°
$V = 571.48$ (18) Å^3
$Z = 1$
$D_x = 1.311$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.5$–12.5°
$\mu = 0.31$ mm^{-1}
$T = 296$ K
Prism, brown
0.50 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.895$, $T_{\max} = 0.940$
2780 measured reflections
2615 independent reflections
1704 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -12 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.122$
$S = 1.01$
2615 reflections
143 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.175P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 1
Selected bond lengthss (Å).

Cl—C2	1.739 (2)	C1—C3$^{\rm i}$	1.543 (3)
O1—C1	1.257 (3)	C2—C3	1.414 (3)
O2—C3	1.227 (2)	N—C8	1.338 (3)
C1—C2	1.381 (3)	N—C4	1.347 (3)

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H1···O1	0.91 (4)	1.81 (4)	2.697 (3)	168 (3)
N—H1···O2$^{\rm i}$	0.91 (4)	2.40 (3)	2.880 (3)	114 (2)
C5—H2···O2$^{\rm ii}$	0.93	2.55	3.345 (4)	143
C9—H6···O1$^{\rm iii}$	0.96	2.59	3.404 (3)	142

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

The H atom attached to the N atom was 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).

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