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Bis(3-methylpyrazolium) chloranilate

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Key indicators

Single-crystal X-ray study
T = 302 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.103
Data-to-parameter ratio = 15.3

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

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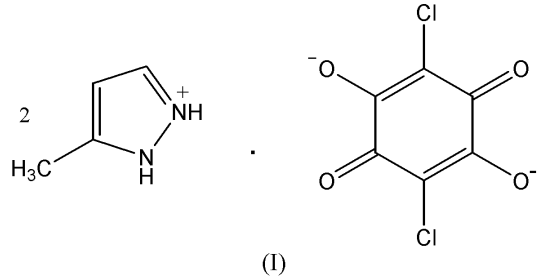
In the title compound, bis(3-methyl-2*H*-pyrazol-1-ium) 2,5-dichloro-3,6-dioxido-1,4-benzoquinone, $2C_4H_7N_2^+\cdot C_6Cl_2O_4^{2-}$, the chloranilate and 3-methylpyrazolium ions are held together by bifurcated N—H···O hydrogen bonds, giving a centrosymmetric chloranilate–3-methylpyrazolium 1:2 unit. The 1:2 units are connected to each other by N—H···O hydrogen bonds, forming a molecular ladder.

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, 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 pyridazine, pyrimidine, pyrazine (Ishida & Kashino, 1999*a*,*b*), pyrazole, imidazole (Ishida & Kashino, 2001), toluidine (Fukunaga *et al.*, 2003), pyrrolidine (Ishida, 2004*a*) and 2,4,6-trimethylpyridine (Ishida, 2004*b*).



(I)

In (I), the chloranilate ion shows a characteristic structure, having four short C—C bonds and two extremely long C—C

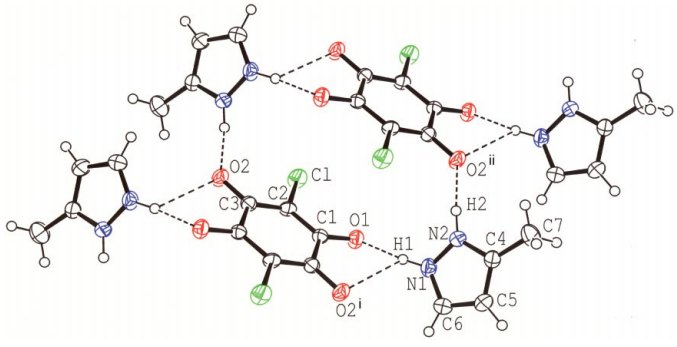


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I), with the atom labeling, showing the formation of a molecular ladder along the *b* axis. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O hydrogen bonds are indicated by dashed lines (symmetry codes are as given in Table 2).

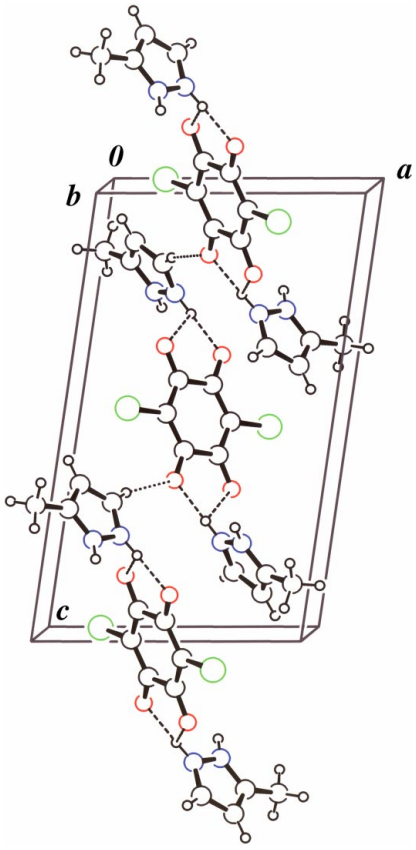


Figure 2
Packing diagram, showing molecular ladders connected by C—H···O hydrogen bonds (shown as dotted lines). N—H···O hydrogen bonds are shown by dashed lines.

bonds (Table 1), which is explainable in terms of the double π system of the anion (Andersen, 1967; Benchekroun & Savariault, 1995). The chloranilate and 3-methylpyrazolium ions are held together by asymmetric bifurcated N—H···O hydrogen bonds (Table 2) to give a centrosymmetric chloranilate–3-methylpyrazolium 1:2 unit. The dihedral angle between the planes of the chloranilate ring and the pyridine ring is 69.92 (15)°. The 1:2 units are connected by N—H···O hydrogen bonds, forming a molecular ladder running parallel to the *b* axis (Fig. 1), similar to that found in the pyrazole salt. Neighboring ladders are connected to each other by C—H···O hydrogen bonds (Fig. 2).

Experimental

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

Crystal data

$2C_4H_7N_2^+\cdot C_6Cl_2O_4^-$
M_r = 373.19
Monoclinic, $P2_1/c$
a = 8.9885 (15) Å
b = 5.7445 (12) Å
c = 15.471 (3) Å
β = 98.749 (15)°
V = 789.5 (3) Å^3
Z = 2
D_x = 1.570 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 11.0–12.5°
μ = 0.44 mm^{-1}
T = 302 K
Prism, dark violet
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.891, T_{max} = 0.917
2566 measured reflections
1807 independent reflections
1142 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 7$
$l = -20 \rightarrow 20$
3 standard reflections
every 97 reflections
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.103
S = 1.04
1807 reflections
118 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 0.238P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cl—C2	1.742 (3)	N2—C4	1.339 (3)
O1—C1	1.251 (3)	C1—C2	1.402 (3)
O2—C3	1.252 (3)	C1—C3^{i}	1.540 (4)
N1—C6	1.317 (3)	C2—C3	1.389 (4)
N1—N2	1.346 (3)	C4—C7	1.471 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.91 (4)	1.75 (4)	2.651 (3)	175 (4)
N1—H1···O2^{i}	0.91 (4)	2.55 (4)	2.970 (3)	109 (3)
N2—H2···O2^{ii}	0.92 (3)	1.81 (3)	2.717 (3)	168 (3)
C6—H4···O1^{iii}	0.93	2.36	3.261 (3)	164

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

H atoms attached to N 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_{iso}(H) values were set at 1.5U_{eq}(C). Aromatic H atoms were also treated as riding, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{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* (MSC, 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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