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Ethylammonium and diethylammonium salts of chloranilic acid

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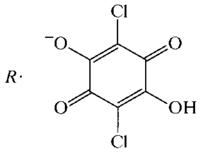
In the crystals of two title salts of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone), namely ethylammonium chloranilate, $C_2H_8N^+\cdot C_6HCl_2O_4^-$, (I), and diethylammonium chloranilate, $C_4H_{12}N^+\cdot C_6HCl_2O_4^-$, (II), the chloranilate ions are present as a hydrogen-bonded dimer which has an inversion center. The ethylammonium and diethylammonium ions link the dimers through N—H···O hydrogen bonds, forming a three-dimensional hydrogen-bond network in (I) and a one-dimensional chain in (II).

Comment

Several hydrogen-bonded complexes of chloranilic acid–amine (1/1) in the solid state were studied by IR (Issa *et al.*, 1991; Habeeb *et al.*, 1995). Habeeb *et al.* (1995) analyzed the IR data on the assumption that the complex consists of a pair of chloranilic acid and amine molecules, and reported that the hydrogen bond formed in the pair varies from an N—H···O to an N···H—O type with decreasing pK_a values of the amines. Recently, we determined the structures of the chloranilic acid–pyrazine (1/1) complex and morpholinium chloranilate (Ishida & Kashino, 1999) and showed that these complexes are not present as a pair of chloranilic acid and amine molecules. In the pyrazine complex, pyrazine and chloranilic acid molecules are alternately arranged to form an O—H···N hydrogen-bond chain. On the other hand, in the morpholinium salt, a chain of chloranilate ions is formed through O—H···O hydrogen bonds and morpholinium ions link the two chains through N—H···O hydrogen bonds, forming the two-dimensional hydrogen-bond network. The complexes of chloranilic acid–amine are, therefore, expected to be a noticeable system in view of our interest in hydrogen-bond patterns and their nature in the solid state. As part of an investigation of this system, we prepared the 1/1 complexes of chloranilic acid with strong bases, ethylamine (pK_a = 10.64) and diethylamine (pK_a = 10.94), and determined their crystal structures.

In (I) and (II), an acid–base interaction involving a proton transfer is observed as expected from the high basicity of the present amines. The molecules of chloranilate ion form a dimer connected by O2—H1···O3^{i} hydrogen bonds [symmetry code: (i) $2-x, 1-y, 2-z$ for (I) and (i) $-x, -y, 1-z$ for (II); Tables 2 and 4]. The H1 atom is also involved in an intramolecular hydrogen bond with O3.



(I) R=EtNH$_3^+$
(II) R=Et$_2$NH$_2^+$

In (I), the ethylammonium ion links the three dimers of chloranilic acid through N—H3···O3^{ii} and N—H4···O4^{iii} hydrogen bonds [symmetry codes: (ii) $1-x, 1-y, 1-z$; (iii) $1-x, 1-y, -z$], and a bifurcated hydrogen bond of N—H2···O1 and N—H2···O4, forming a three-dimensional hydrogen-bond network. A weak C—H···O interaction between the methyl group of the cation and the anion is observed [C8—H7 1.01 (3), H7···O1 2.56 (3), C8···O1 3.340 (4) Å and C8—H7···O1 134 (2)°], which may stabilize the orientation of C8—C7 bond. In (II), the diethylammonium ions related by an inversion center link the two dimers of chloranilic acid through a bifurcated hydrogen bond of N—H2···O1 and N—H2···O4, and an N—H3···O4^{i} hydrogen bond [as in (i) for (I) above], forming an infinite chain along [211]. The shortest contact between the chains is O2···H4^{iv} 2.63 (3) Å [C7—H4 0.97 (3), O2···C7^{iv} 3.483 (4) Å, O2···H4^{iv}—C7^{iv} 146 (2)°; symmetry code: (iv) $1-x, -y, 2-z$].

The anions form dimers in both salts, but the O2···O3 contact distance between the anions in the dimer in (I), 2.797 (2) Å, is rather longer than in (II), 2.677 (2) Å. The O3 atom in (I) is linked to the cation through a hydrogen bond, while the O3 atom in (II) does not participate in such an additional hydrogen bond. This may cause the difference in the O2···O3 distance between (I) and (II).

Experimental

Crystals of the title complexes were prepared by slow evaporation from acetonitrile solutions of chloranilic acid with ethylamine or diethylamine (molar ratio 1:1) at room temperature.

Compound (I)

Crystal data

$C_2H_8N^+\cdot C_6HO_4Cl_2^-$
$M_r = 254.07$
Triclinic, $P\bar{1}$
$a = 7.201$ (2) Å
$b = 10.348$ (2) Å
$c = 7.190$ (2) Å
$\alpha = 95.59$ (2)°
$\beta = 92.95$ (2)°
$\gamma = 98.47$ (2)°
$V = 526.3$ (2) Å^3

$Z = 2$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.6$–11.5°
$\mu = 0.608$ mm^{-1}
$T = 303$ K
Plate, brown
0.30 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.898$, $T_{\rm max} = 0.941$
2620 measured reflections
2425 independent reflections
1402 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -9 \rightarrow 9$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.050$
$S = 1.29$
2424 reflections
172 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.50$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cl1—C2	1.725 (2)	C1—C6	1.540 (3)
Cl2—C5	1.737 (2)	C2—C3	1.334 (3)
O1—C1	1.215 (2)	C3—C4	1.502 (3)
O2—C3	1.336 (3)	C4—C5	1.396 (3)
O3—C4	1.251 (2)	C5—C6	1.394 (3)
O4—C6	1.246 (2)	N—C7	1.490 (3)
C1—C2	1.453 (3)	C7—C8	1.497 (4)
N—C7—C8	111.0 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H1$\cdots$O3$^{\rm i}$	0.92 (3)	2.10 (3)	2.797 (2)	131 (3)
O2—H1$\cdots$O3	0.92 (3)	2.04 (3)	2.797 (2)	120 (2)
N—H2$\cdots$O1	0.89 (3)	2.16 (3)	2.953 (3)	147 (2)
N—H2$\cdots$O4	0.89 (3)	2.26 (3)	2.932 (3)	132 (2)
N—H3$\cdots$O3$^{\rm ii}$	1.06 (3)	1.87 (3)	2.883 (3)	158 (2)
N—H4$\cdots$O4$^{\rm iii}$	0.96 (3)	1.94 (3)	2.813 (3)	152 (3)

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

Compound (II)

Crystal data

$C_4H_{12}N^+\cdot C_6HO_4Cl_2^-$
$M_r = 282.12$
Triclinic, $P\overline{1}$
$a = 9.159$ (3) Å
$b = 9.617$ (2) Å
$c = 8.979$ (3) Å
$\alpha = 108.17$ (2)°
$\beta = 111.27$ (3)°
$\gamma = 103.78$ (2)°
$V = 642.8$ (5) Å^3
$Z = 2$
$D_x = 1.458$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.7$–$12.4°$
$\mu = 0.506$ mm^{-1}
$T = 302$ K
Prismatic, dark purple
0.40 × 0.30 × 0.30 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.839$, $T_{\rm max} = 0.859$
3144 measured reflections
2958 independent reflections
1793 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -11 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.053$
$wR(F^2) = 0.091$
$S = 1.64$
2956 reflections
206 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00012|F_o|^2]$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.55$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.61$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Cl1—C2	1.715 (2)	C2—C3	1.336 (3)
Cl2—C5	1.725 (2)	C3—C4	1.501 (3)
O1—C1	1.215 (2)	C4—C5	1.411 (3)
O2—C3	1.325 (2)	C5—C6	1.387 (3)
O3—C4	1.235 (2)	N—C7	1.488 (4)
O4—C6	1.255 (2)	N—C9	1.492 (3)
C1—C2	1.454 (3)	C7—C8	1.492 (5)
C1—C6	1.534 (3)	C9—C10	1.487 (5)
N—C7—C8	110.9 (3)	N—C9—C10	111.2 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H1$\cdots$O3$^{\rm i}$	0.82 (3)	1.94 (3)	2.677 (2)	148 (3)
O2—H1$\cdots$O3	0.82 (3)	2.23 (3)	2.649 (2)	112 (3)
N—H2$\cdots$O4	0.97 (3)	2.00 (3)	2.910 (3)	155 (2)
N—H2$\cdots$O1	0.97 (3)	2.33 (3)	2.979 (3)	124 (2)
N—H3$\cdots$O4$^{\rm ii}$	0.93 (2)	1.95 (3)	2.838 (3)	160 (2)

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

H atoms were found in a difference Fourier map and were refined isotropically; C—H = 0.94 (3)–1.14 (2), N—H = 0.89 (3)–1.06 (3) and O—H = 0.92 (3) Å for (I), and C—H = 0.94 (4)–1.05 (4), N—H = 0.93 (2) and 0.97 (3), and O—H = 0.82 (3) Å for (II).

For (I) and (II), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*; program(s) used to solve structure: *SAPI*91 (Fan, 1991) for (I) and *SIR*92 (Altomare *et al.*, 1993) for (II).

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