

1:2 Complexes of chloranilic acid with pyrazole and imidazole, and the acetonitrile solvate of a 1:1 complex with imidazole

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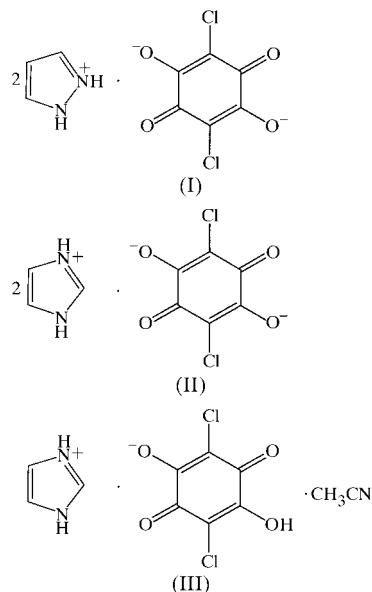
2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) forms $X-H\cdots Y$ ($X, Y = N$ or O) and $C-H\cdots Cl$ hydrogen bonds with pyrazole and imidazole to afford bis(pyrazolium) dichloroanilate and bis(imidazolium) dichloroanilate, (I) and (II), both $2C_3H_5N_2^+ \cdot C_6Cl_2O_4^{2-}$, and imidazolium chloroanilate acetonitrile solvate, $C_3H_5N_2^+ \cdot C_6HCl_2O_4^- \cdot C_2H_3N$, (III). Their crystal structures demonstrate three novel supramolecular architectures based on supramolecular synthons to build a ladder, (I), a two-dimensional network, (II), and a flat ribbon, (III).

Comment

2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone, a strong dibasic acid endowed with hydrogen-bond donor as well as acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with polarizable cations. In fact, our crystallographic studies on 1:1 and 1:2 complexes of chloranilic acid (CLA) with amines revealed various types of hydrogen-bonding patterns formed between CLA and amine, as well as between CLAs (Ishida & Kashino, 1999*a,b,c*, 2000). Recently, Zaman *et al.* (1999, 2000) synthesized 1:1 complexes of CLA with dipyridyl derivatives [4,4'-bipyridine, 1,2-bis(2-pyridyl)ethylene, and 2,2', 3,3'- and 4,4'-dipyridylacetylenes] and revealed the crystal structures by X-ray analysis. The structures of the complexes exhibit supramolecular architectures, such as linear chains, zigzag tapes and square grids, which are composed of supramolecular synthons (Desiraju, 1995, 1997; Nangia & Desiraju, 1998), (1) and (2), formed by asymmetric bifurcated intermolecular hydrogen bonds.

Here, we have used pyrazole (PYZ) and imidazole (IMZ) as counter-cations for CLA and realised molecular networks based on hydrogen bonds in the 1:2 complexes of CLA with pyrazole and imidazole, $2[PYZ]^+ \cdot [CLA]^{2-}$, (I), and $2[IMZ]^+ \cdot [CLA]^{2-}$, (II), and the 1:1 complex with imidazole acetonitrile monosolvate, $[IMZ]^+ \cdot [CLA]^- \cdot CH_3CN$, (III). The

structures of these crystals demonstrate three unique supramolecular assemblies based on synthons (1) and (2) to build a ladder, (I), a two-dimensional network, (II), and a flat ribbon, (III). This paper describes the new robust motifs in the crystal structures composed of simple azoles.



The asymmetric units of (I), (II) and (III) are composed of $C_3H_5N_2^+ \cdot 0.5C_6Cl_2O_4^{2-}$, $C_3H_5N_2^+ \cdot 0.5C_6Cl_2O_4^{2-}$ and $C_3H_5N_2^+ \cdot C_6HCl_2O_4^- \cdot C_2H_3N$, respectively. In all three complexes, asymmetric interionic hydrogen bonds between the N atoms of the cation and the two O atoms of the anion are observed. In addition, short $N-H\cdots O$ hydrogen bonds are observed between the cation and the anion. In (I), the CLA ion forms a ladder running parallel to the b axis, both sides of which are connected by pyrazolium ions related by an inversion center *via* an $N2-H2\cdots O2$ hydrogen bond and an asymmetric bifurcated $N1-H1\cdots O1$ and $N1-H1\cdots O2$ hydrogen bond (Fig. 1 and Table 2). The dihedral angle between the planes of the anion and the cation is 111° .

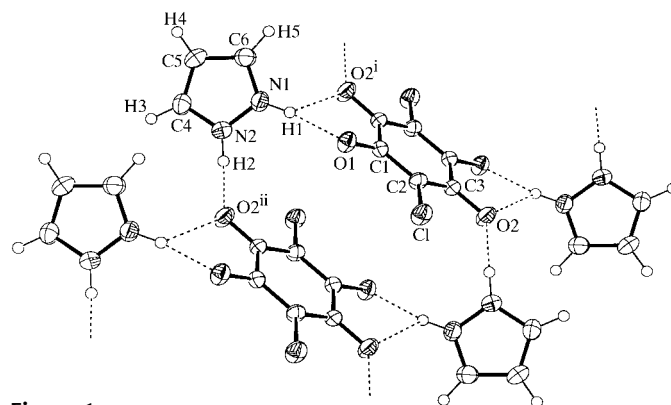


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) showing the atomic labelling and an anion ladder held by cations *via* $N-H\cdots O$ hydrogen bonds. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines (the symmetry codes are as in Table 2).

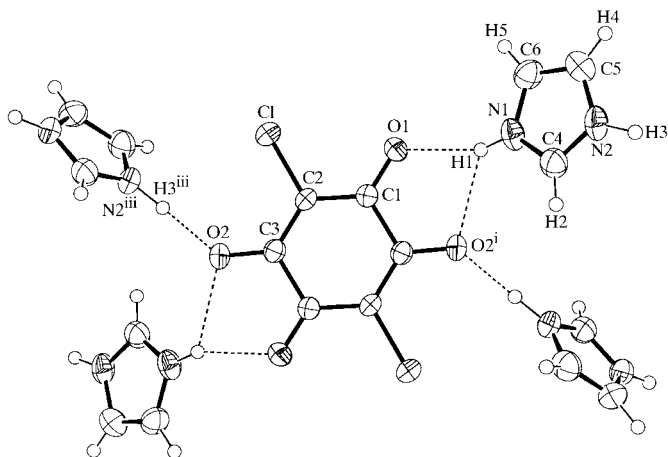


Figure 2
ORTEP-3 (Farrugia, 1997) drawing of (II) showing the atomic labelling and hydrogen-bonding scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines [the symmetry codes are as in Table 4 with the addition of (iii) $1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$].

In (II), the anions and cations are connected by a bifurcated $N1-H1 \cdots O1$ and $N1-H1 \cdots O2$ hydrogen bond, and a short $N2-H3 \cdots O2$ hydrogen bond (Fig. 2 and Table 4), forming a two-dimensional hydrogen-bond network parallel to the (102) plane (Fig. 3). The dihedral angle between the planes of the anion and the cation is 146° . In (III), the CLA ion acts as a hydrogen donor as well as an acceptor. All constituent molecules are planar and parallel to the (101) plane and the imidazolium ion and the two anions are connected by an $N1-H2 \cdots O1$ hydrogen bond and a bifurcated $N2-H4 \cdots O2$ and $N2-H4 \cdots O3$ hydrogen bond (Fig. 4). Acetonitrile also

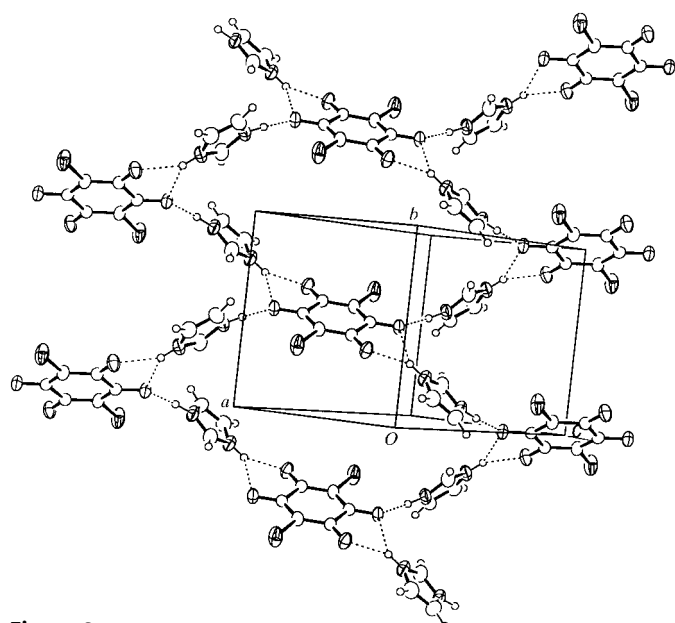


Figure 3
Part of the crystal structure of (II) showing a two-dimensional hydrogen-bonded network formed by anions and cations via $N-H \cdots O$ hydrogen bonds, which are indicated by dashed lines.

connects the anions through a weak $C11-H7 \cdots Cl2$ interaction and an $O4-H1 \cdots N3$ hydrogen bond. Atom H1 also participates in an intramolecular $O4-H1 \cdots O1$ hydrogen bond (Table 6). The $C11 \cdots O3$ [$3.751(4) \text{ \AA}$] and $H7 \cdots O3$ [$2.91(4) \text{ \AA}$] distances are long but the $C11-H7 \cdots O3$ angle of $160(4)^\circ$ is essentially linear, suggesting that a weak $C-H \cdots O$ interaction (Desiraju & Steiner, 1999) exists between the anion and the acetonitrile molecule.

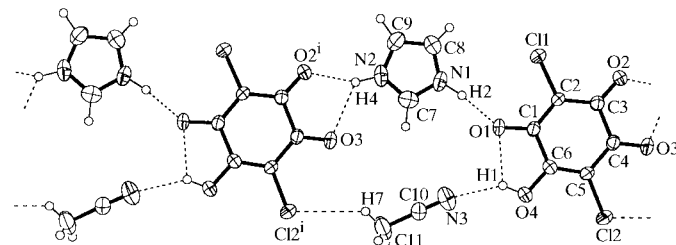


Figure 4
ORTEP-3 (Farrugia, 1997) drawing of a molecular ribbon of (III) with the atomic labelling. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines (the symmetry code is as in Table 6).

Experimental

Prismatic crystals of (I) and (II) were obtained by slow evaporation from aqueous solutions of chloranilic acid with pyrazole or imidazole (molar ratio 1:2) at room temperature. Compound (III) was prepared by reacting imidazole and chloranilic acid (molar ratio 1:1) in acetonitrile and prismatic crystals were obtained by recrystallization from a methanol solution.

Compound (I)

Crystal data

$2C_3H_5N_2^+ \cdot C_6Cl_2O_4^{2-}$
 $M_r = 345.14$
Monoclinic, $P2_1/c$
 $a = 8.043(3) \text{ \AA}$
 $b = 5.459(3) \text{ \AA}$
 $c = 15.740(4) \text{ \AA}$
 $\beta = 92.73(2)^\circ$
 $V = 690.3(4) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.660 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.9-12.5^\circ$
 $\mu = 0.494 \text{ mm}^{-1}$
 $T = 292 \text{ K}$
Prismatic, brown
 $0.45 \times 0.40 \times 0.30 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
Absorption correction: ψ scans
(North *et al.*, 1968)
 $T_{\min} = 0.77, T_{\max} = 0.86$
2127 measured reflections
1591 independent reflections
1299 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -1 \rightarrow 10$
 $k = 0 \rightarrow 7$
 $l = -20 \rightarrow 20$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.050$
 $wR(F^2) = 0.076$
 $S = 1.43$
1590 reflections
121 parameters
All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + 0.00019|F_o|^2]$

$(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
Extinction correction:
Zachariasen (1967)
Extinction coefficient:
 $3.23(8) \times 10^{-5}$

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

C1—C2	1.7409 (18)	C1—C2	1.403 (2)
O1—C1	1.247 (2)	C1—C3 ⁱ	1.541 (2)
O2—C3	1.2537 (19)	C2—C3	1.390 (2)
N1—N2	1.335 (2)	C4—C5	1.366 (3)
N1—C6	1.333 (2)	C5—C6	1.376 (3)
N2—C4	1.336 (2)		

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

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O1	0.88 (3)	1.82 (3)	2.689 (2)	168 (3)
N1—H1...O2 ⁱ	0.88 (3)	2.42 (3)	2.916 (2)	116 (2)
N2—H2...O2 ⁱⁱ	0.91 (2)	1.74 (2)	2.638 (2)	167 (2)

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

Compound (II)

Crystal data

$2C_3H_5N_2^+ \cdot C_6Cl_2O_4^{2-}$
 $M_r = 345.14$
 Monoclinic, $P2_1/c$
 $a = 7.547 (2) \text{ \AA}$
 $b = 8.1565 (15) \text{ \AA}$
 $c = 11.750 (4) \text{ \AA}$
 $\beta = 101.10 (3)^\circ$
 $V = 709.7 (3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.615 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.7\text{--}12.2^\circ$
 $\mu = 0.481 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Prismatic, brown
 $0.50 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scans
 (North *et al.*, 1968)
 $T_{\min} = 0.85$, $T_{\max} = 0.91$
 2141 measured reflections
 1634 independent reflections
 1172 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -1 \rightarrow 9$
 $k = 0 \rightarrow 10$
 $l = -15 \rightarrow 15$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.051$
 $wR(F^2) = 0.073$
 $S = 1.35$
 1634 reflections
 121 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + 0.00011|F_o|^2]$

$(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
 Extinction correction:
 Zachariasen (1967)
 Extinction coefficient:
 $1.39 (5) \times 10^{-5}$

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

C1—C2	1.738 (2)	N2—C5	1.364 (3)
O1—C1	1.243 (2)	C1—C2	1.410 (3)
O2—C3	1.258 (2)	C1—C3 ⁱ	1.540 (3)
N1—C4	1.315 (3)	C2—C3	1.385 (3)
N1—C6	1.362 (3)	C5—C6	1.335 (3)
N2—C4	1.315 (3)		

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

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O1	0.88 (3)	1.98 (3)	2.790 (2)	152 (3)
N1—H1...O2 ⁱ	0.88 (3)	2.30 (3)	2.924 (2)	127 (2)
N2—H3...O2 ⁱⁱ	0.99 (3)	1.72 (3)	2.712 (2)	175 (3)

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

Compound (III)

Crystal data

$C_3H_5N_2^+ \cdot C_6HCl_2O_4^- \cdot C_2H_3N$
 $M_r = 318.12$
 Triclinic, $P\bar{1}$
 $a = 9.3895 (19) \text{ \AA}$
 $b = 9.628 (2) \text{ \AA}$
 $c = 8.214 (2) \text{ \AA}$
 $\alpha = 95.86 (2)^\circ$
 $\beta = 99.82 (2)^\circ$
 $\gamma = 111.156 (16)^\circ$
 $V = 671.4 (3) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.573 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.7\text{--}12.3^\circ$
 $\mu = 0.499 \text{ mm}^{-1}$
 $T = 297 \text{ K}$
 Prismatic, dark brown
 $0.50 \times 0.30 \times 0.25 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scans
 (North *et al.*, 1968)
 $T_{\min} = 0.84$, $T_{\max} = 0.88$
 3283 measured reflections
 3093 independent reflections
 2048 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 12$
 $k = -12 \rightarrow 11$
 $l = -10 \rightarrow 10$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.052$
 $wR(F^2) = 0.063$
 $S = 1.37$
 3093 reflections
 217 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + 0.00006|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

Table 5
Selected geometric parameters (Å) for (III).

C11—C2	1.7350 (19)	N3—C10	1.114 (3)
C12—C5	1.724 (2)	C1—C2	1.397 (3)
O1—C1	1.253 (2)	C1—C6	1.498 (3)
O2—C3	1.245 (2)	C2—C3	1.402 (3)
O3—C4	1.218 (2)	C3—C4	1.549 (3)
O4—C6	1.329 (2)	C4—C5	1.446 (3)
N1—C7	1.326 (3)	C5—C6	1.342 (3)
N1—C8	1.354 (3)	C8—C9	1.328 (3)
N2—C7	1.307 (3)	C10—C11	1.443 (4)
N2—C9	1.365 (3)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
O4—H1...N3	0.86 (3)	2.08 (3)	2.827 (3)	145 (3)
O4—H1...O1	0.86 (3)	2.11 (3)	2.613 (2)	116 (2)
N1—H2...O1	0.94 (3)	1.78 (3)	2.703 (2)	171 (3)
N2—H4...O2 ⁱ	0.95 (3)	1.89 (3)	2.773 (2)	154 (2)
N2—H4...O3 ⁱ	0.95 (3)	2.31 (3)	2.974 (3)	127 (2)
C11—H7...Cl2 ⁱ	0.88 (4)	2.81 (5)	3.507 (4)	136 (4)

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

H atoms were found in a difference Fourier map and were refined isotropically. Refined distances: C–H = 0.93 (2)–0.99 (2) Å and N–H = 0.88 (3) and 0.91 (2) Å for (I); C–H = 0.92 (2)–0.95(2) Å and N–H = 0.88 (3) and 0.99 (3) Å for (II); C–H = 0.81 (3)–0.99 (3) Å, N–H = 0.94 (3) and 0.95 (3) Å, and O–H = 0.86 (3) Å for (III).

For all compounds, data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1164). Services for accessing these data are described at the back of the journal.

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