



Crystal structures of three hydrogen-bonded 1:2 compounds of chloranilic acid with 2-pyridone, 3-hydroxypyridine and 4-hydroxypyridine

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Received 17 September 2017

Accepted 21 September 2017

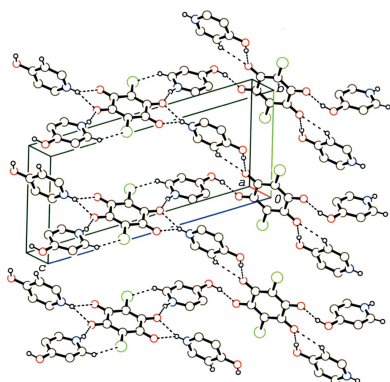
Edited by A. J. Lough, University of Toronto, Canada

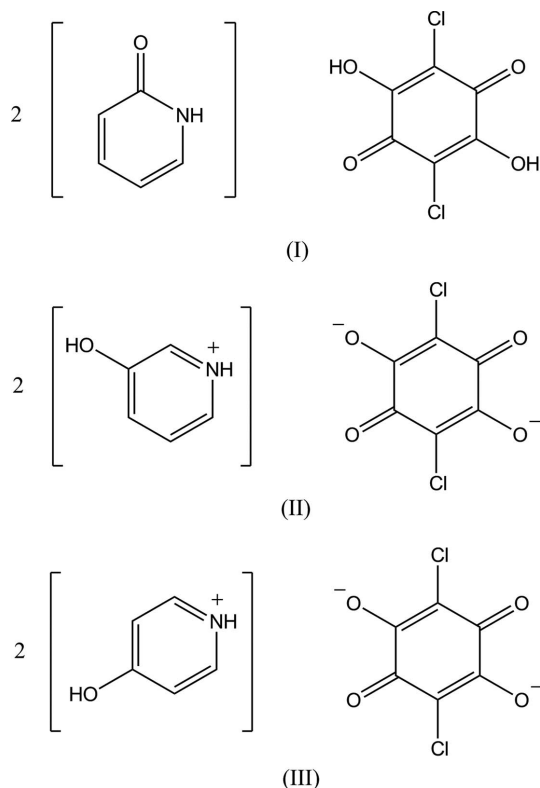
Keywords: crystal structure; chloranilic acid; 2-pyridone; 3-hydroxypyridine; 4-hydroxypyridine; hydrogen bond.**CCDC references:** 1575722; 1575721; 1575720**Supporting information:** this article has supporting information at journals.iucr.org/e

The crystal structures of the 1:2 compounds of chloranilic acid (systematic name: 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) with 2-pyridone, 3-hydroxypyridine and 4-hydroxypyridine, namely, bis(2-pyridone) chloranilic acid, $2C_5H_5NO \cdot C_6H_2Cl_2O_4$, (I), bis(3-hydroxypyridinium) chloranilate, $2C_5H_6NO^+ \cdot C_6Cl_2O_4^{2-}$, (II), and bis(4-hydroxypyridinium) chloranilate, $2C_5H_6NO^+ \cdot C_6Cl_2O_4^{2-}$, (III), have been determined at 120 K. In the crystal of (I), the base molecule is in the lactam form and no acid–base interaction involving H-atom transfer is observed. The acid molecule lies on an inversion centre and the asymmetric unit consists of one half-molecule of chloranilic acid and one 2-pyridone molecule, which are linked *via* a short O–H...O hydrogen bond. 2-Pyridone molecules form a head-to-head dimer *via* a pair of N–H...O hydrogen bonds, resulting in a tape structure along [201]. In the crystals of (II) and (III), acid–base interactions involving H-atom transfer are observed and the divalent cations lie on an inversion centre. The asymmetric unit of (II) consists of one half of a chloranilate anion and one 3-hydroxypyridinium cation, while that of (III) comprises two independent halves of anions and two 4-hydroxypyridinium cations. The primary intermolecular interaction in (II) is a bifurcated O–H...(O,O) hydrogen bond between the cation and the anion. The hydrogen-bonded units are further linked *via* N–H...O hydrogen bonds, forming a layer parallel to the *bc* plane. In (III), one anion is surrounded by four cations *via* O–H...O and C–H...O hydrogen bonds, while the other is surrounded by four cations *via* N–H...O and C–H...Cl hydrogen bonds. These interactions link the cations and the anions into a layer parallel to (301).

1. Chemical context

Chloranilic acid, a dibasic acid with hydrogen-bond donor and acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with various pyridine derivatives, as well as a model compound for investigating hydrogen transfer motions in O–H...N and N–H...O hydrogen-bond systems (Zaman *et al.*, 2004; Seliger *et al.*, 2009; Asaji *et al.* 2010). In the present study, we have prepared three 1:2 compounds of chloranilic acid with 2-pyridone, 3-hydroxypyridine and 4-hydroxypyridine in order to extend our study of *D*–H...*A* hydrogen bonding (*D* = N, O or C; *A* = N, O or Cl) in chloranilic acid–substituted-pyridine systems (Gotoh *et al.*, 2009*a,b*, 2010). The crystal structure of the 1:1 compound of chloranilic acid with 3-hydroxypyridine, namely, 3-hydroxypyridinium hydrogen chloranilate monohydrate, has been reported (Gotoh & Ishida, 2009).





2. Structural commentary

In compound (I), the base molecule is in the lactam form and no acid–base interaction involving H-atom transfer is observed (Fig. 1). The acid molecule lies on an inversion centre and the asymmetric unit consists of one-half acid molecule and one base molecule, which are linked *via* a short O–H...O hydrogen bond (O2–H2...O3; Table 1). The dihedral angle between the acid ring and the base ring is 37.82 (5)°.

In compound (II), an acid–base interaction involving H-atom transfer is observed. The chloranilate anion is located on an inversion centre and the asymmetric unit contains one-half anion molecule and one cation molecule. The primary intermolecular interaction between the cation and the anion is a bifurcated O–H...O(O) hydrogen bond (O3–H3...O2

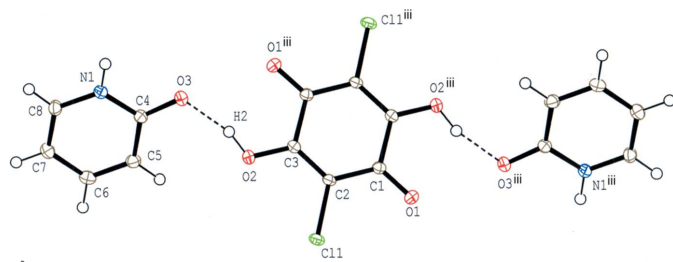


Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. O–H...O hydrogen bonds are shown as dashed lines. [Symmetry code: (iii) $-x + 1, -y + 1, -z + 1$.]

Table 1
Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O2–H2...O3	0.901 (15)	1.627 (16)	2.4989 (11)	161.9 (19)
N1–H1...O3 ⁱ	0.893 (16)	1.996 (17)	2.8743 (12)	167.6 (16)
C7–H7...Cl1 ⁱⁱ	0.95	2.79	3.5122 (13)	134

Symmetry codes: (i) $-x + 2, y, -z + \frac{3}{2}$; (ii) $-x + 2, -y, -z + 1$.

and O3–H3...O1ⁱ; symmetry code as in Table 2) to afford a centrosymmetric 1:2 aggregate of the anion and the cation (Fig. 2). The dihedral angle between the acid ring and the base ring is 72.69 (5)°.

The compound (III) crystallizes with two independent halves of chloranilate anions and two 4-hydroxypyridinium cations in the asymmetric unit (Fig. 3). Although both anions lie on an inversion centre, the hydrogen-bonding schemes around the anions are quite different (Fig. 4); one anion is surrounded by four cations *via* O–H...O and C–H...O hydrogen bonds (O5–H5...O1ⁱ, O6–H6...O2 and C13–H13...O2; symmetry code as in Table 3), while the other is surrounded by four cation *via* N–H...O and C–H...Cl hydrogen bonds (N1–H1...O4, N2–H2...O4ⁱⁱ, N2–H2...O3ⁱⁱⁱ and C7–H7...Cl2; Table 3).

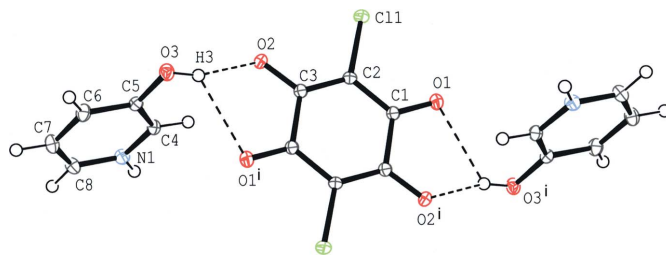


Figure 2
The molecular structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. O–H...O hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.]

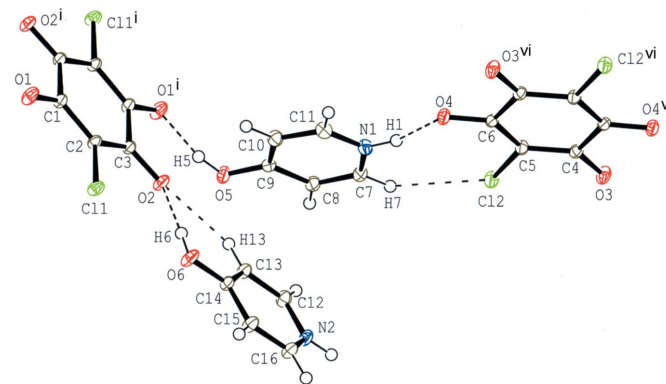


Figure 3
The molecular structure of compound (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. O–H...O, N–H...O, C–H...Cl and C–H...O hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x, -y, -z$; (vi) $-x + 3, -y, -z + 1$.]

Table 2
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3···O2	0.852 (17)	1.803 (17)	2.6277 (12)	162.5 (16)
O3—H3···O1 ⁱ	0.852 (17)	2.438 (17)	2.9738 (12)	121.6 (14)
N1—H1···O2 ⁱⁱ	0.889 (17)	1.807 (17)	2.6684 (12)	162.6 (16)
C8—H8···O1 ⁱⁱⁱ	0.95	2.45	3.1481 (13)	130

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x - 1, y, z - 1$.

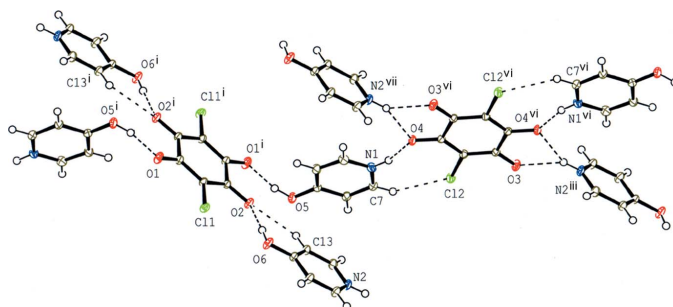


Figure 4
A partial packing diagram for compound (III) around two independent chloranilate anions. O—H···O, N—H···O, C—H···Cl and C—H···O hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x, -y, -z$; (iii) $-x + 3, -y + 1, -z + 1$; (vi) $-x + 3, -y, -z + 1$; (vii) $x, y - 1, z$.]

3. Supramolecular features

In the crystal of compound (I), two adjacent 2-pyridone molecules, which are related by a twofold rotation axis, form a head-to-head dimer *via* a pair of N—H···O hydrogen bonds (N1—H1···O3ⁱ; symmetry code as in Table 1), as observed in various cocrystals of 2-pyridone (Odani & Matsumoto, 2002).

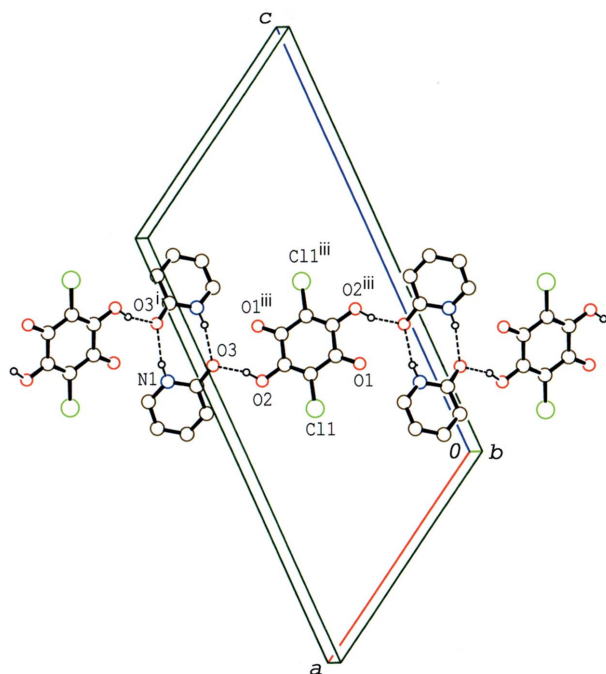


Figure 5
A packing diagram for compound (I), showing the tape structure formed by O—H···O and N—H···O hydrogen bonds (dashed lines). H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $-x + 2, y, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 1, -z + 1$.]

Table 3
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H5···O1 ⁱ	0.905 (17)	1.640 (17)	2.5208 (13)	163.2 (17)
O6—H6···O2	0.852 (17)	1.800 (17)	2.6510 (13)	177.3 (18)
N1—H1···O4	0.919 (17)	1.810 (17)	2.7000 (13)	162.3 (16)
N2—H2···O4 ⁱⁱ	0.876 (18)	2.156 (17)	2.9603 (14)	152.3 (15)
N2—H2···O3 ⁱⁱⁱ	0.876 (18)	2.176 (17)	2.8384 (14)	132.1 (14)
C7—H7···Cl2	0.95	2.81	3.4540 (12)	126
C12—H12···O3 ^{iv}	0.95	2.32	3.1541 (14)	146
C13—H13···O2	0.95	2.49	3.1685 (14)	128
C16—H16···Cl1 ^v	0.95	2.77	3.4427 (12)	128

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y + 1, z$; (iii) $-x + 3, -y + 1, -z + 1$; (iv) $-x + 2, -y + 1, -z + 1$; (v) $-x + 2, -y + 1, -z$.

The acid and base molecules form an undulating tape structure running along [201] through the above-mentioned O—H···O and N—H···O hydrogen bonds (Fig. 5). The tapes are stacked along the *b* axis into a layer structure through a π – π interaction between the pyridine rings [centroid-to-centroid distance = 3.7005 (6) Å and interplanar spacing = 3.4239 (4) Å] and a short C···C contact [C2···C3^{iv} = 3.3056 (13) Å; symmetry code: (iv) $x, y + 1, z$]. A weak C—H···Cl interaction formed between the acid and base molecules (C7—H7···Cl1ⁱⁱ; Table 1) links the layers. The O—H···O hydrogen bond between the acid and base molecules is short [O2···O3 = 2.4989 (11) Å], suggesting possible disorder of the H atom in the hydrogen bond, but no distinct evidence of the disorder was observed in the difference Fourier map, nor from the molecular geometry.

In the crystal of (II), the cation–anion units are further connected by N—H···O (N1—H1···O2ⁱⁱ; symmetry code as in Table 2 and Fig. 6), forming a layer expanding parallel to the *bc* plane (Fig. 7). Adjacent layers are connected to each other with a C—H···O hydrogen bond (C8—H8···O1ⁱⁱⁱ; Table 2) and a short O···N contact [O3···N1^{vi} = 3.0430 (12) Å; symmetry code: (vi) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$].

In the crystal of (III), the above-mentioned O—H···O, N—H···O, C—H···O and C—H···Cl hydrogen bonds link the

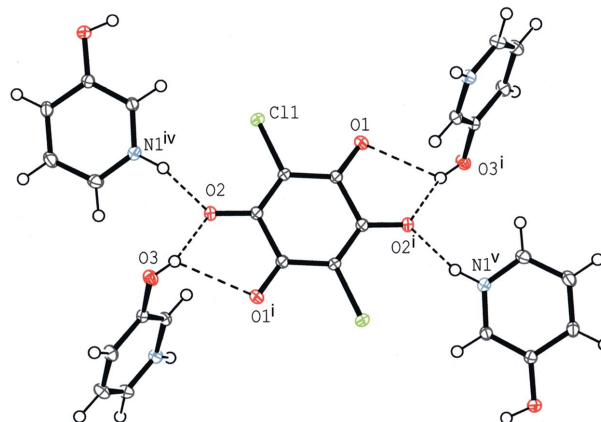


Figure 6
A partial packing diagram for compound (II) around the chloranilate anion. O—H···O and N—H···O hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.]

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$2C_5H_5NO \cdot C_6H_2Cl_2O_4$	$2C_5H_6NO^+ \cdot C_6Cl_2O_4^{2-}$	$2C_5H_6NO^+ \cdot C_6Cl_2O_4^{2-}$
M_r	399.19	399.19	399.19
Crystal system, space group	Monoclinic, $P2/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	120	120	120
a, b, c (Å)	11.9402 (7), 3.7005 (2), 21.7919 (13)	8.3659 (6), 8.5492 (6), 11.7087 (8)	5.49136 (13), 8.2195 (4), 18.1382 (9)
α, β, γ (°)	90, 121.278 (2), 90	90, 106.968 (3), 90	102.177 (3), 93.952 (3), 95.316 (4)
V (Å ³)	822.92 (9)	800.98 (9)	793.52 (6)
Z	2	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.43	0.45	0.45
Crystal size (mm)	0.39 × 0.36 × 0.21	0.21 × 0.20 × 0.12	0.35 × 0.25 × 0.12
Data collection			
Diffractometer	Rigaku R-Axis RAPIDII	Rigaku R-Axis RAPIDII	Rigaku R-Axis RAPIDII
Absorption correction	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)	Numerical (<i>NUMABS</i> ; Higashi, 1999)	Numerical (<i>NUMABS</i> ; Higashi, 1999)
T_{min} , T_{max}	0.804, 0.913	0.903, 0.948	0.890, 0.948
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22767, 2401, 2316	15315, 2329, 2166	12373, 4597, 4124
R_{int}	0.013	0.017	0.036
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.703	0.703	0.703
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.076, 1.06	0.028, 0.075, 1.07	0.030, 0.080, 1.07
No. of reflections	2401	2329	4597
No. of parameters	124	124	247
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.49, -0.24	0.52, -0.20	0.75, -0.34

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2010) and *PLATON* (Spek, 2009).

cations and anions into a layer parallel to (301) (Fig. 8). Adjacent layers are further linked *via* weak C—H...O and C—H...Cl interactions (C12—H12...O3^{iv} and C16—H16...Cl^{iv}; symmetry codes as given in Table 3).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, last update May 2017; Groom *et al.*, 2016) for organic crystals of chloranilic acid with substituted pyridines (except for di-, tri- and tetrapyridine derivatives) gave 32 hits. Of these, crystal structures of 16 compounds of chloranilic acid with methyl-substituted pyridines (Adam *et al.*, 2010; Łuczyńska *et al.*, 2016; Molčanov & Kojić-Prodić, 2010, and references therein), three compounds of carbamoyl-substituted pyridines (Gotoh *et al.*, 2009a), three compounds of carboxy-substituted pyridines (Gotoh *et al.*, 2009b, and references therein) and three compounds of cyano-substituted pyridines (Gotoh & Ishida, 2012, and references therein) were reported.

5. Synthesis and crystallization

Single crystals of compound (I) were obtained by slow evaporation from an ethanol solution (120 ml) of chloranilic acid (350 mg) with 2-hydroxypyridine (340 mg) at room

temperature. Crystals of compound (II) were obtained by slow evaporation from a methanol solution (400 ml) of chloranilic acid (170 mg) with 3-hydroxypyridine (160 mg) at room temperature. Crystals of compound (III) were obtained by slow diffusion of a methanol solution (20 ml) of 4-hydroxypyridine (160 mg) into an acetonitrile solution (200 ml) of chloranilic acid (170 mg) at room temperature.

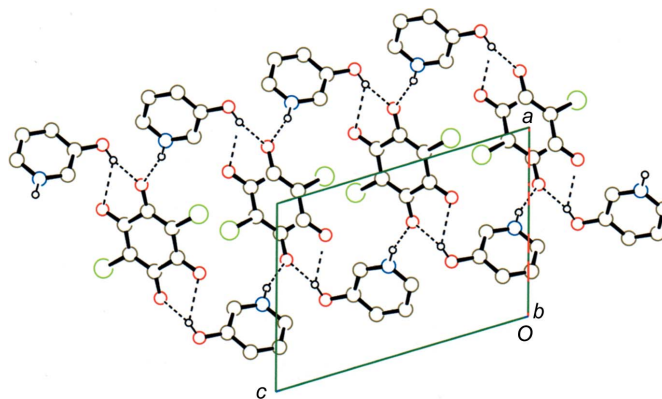


Figure 7
A packing diagram for compound (II), viewed along the b axis, showing the layer structure formed by O—H...O and N—H...O hydrogen bonds (dashed lines). H atoms not involved in the interactions have been omitted.

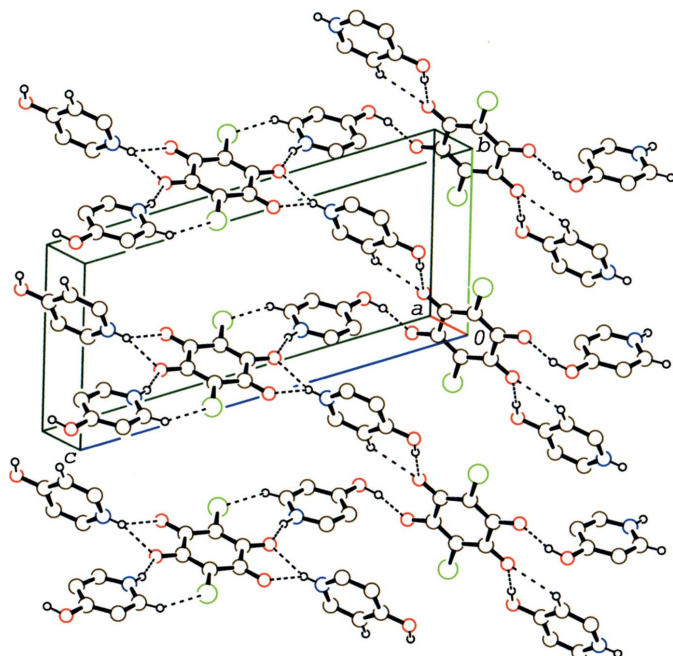


Figure 8

A packing diagram for compound (III), showing the hydrogen-bonded network in the layer. O—H···O, N—H···O, C—H···Cl and C—H···O hydrogen bonds are shown as dashed lines. H atoms not involved in the hydrogen bonds have been omitted.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms in compounds (I)–(III) were found in difference Fourier maps. The positions of

O- and N-bound H atoms were refined freely, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O or N})$. C-bound H atoms were positioned geometrically (C—H = 0.95 Å) and were treated as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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supporting information

Acta Cryst. (2017). E73, 1546-1550 [https://doi.org/10.1107/S2056989017013536]

Crystal structures of three hydrogen-bonded 1:2 compounds of chloranilic acid with 2-pyridone, 3-hydroxypyridine and 4-hydroxypyridine

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Computing details

For all structures, data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO* (Rigaku, 2006); data reduction: *RAPID-AUTO* (Rigaku, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012). Software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010), *PLATON* (Spek, 2009) for (I); *CrystalStructure* (Rigaku, 2010) and *PLATON* (Spek, 2009) for (II), (III).

Bis[pyridin-2(1*H*)-one] 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (I)

Crystal data

$2\text{C}_5\text{H}_5\text{NO}\cdot\text{C}_6\text{H}_2\text{Cl}_2\text{O}_4$

$M_r = 399.19$

Monoclinic, *P2/c*

$a = 11.9402$ (7) Å

$b = 3.7005$ (2) Å

$c = 21.7919$ (13) Å

$\beta = 121.278$ (2)°

$V = 822.92$ (9) Å³

$Z = 2$

$F(000) = 408.00$

$D_x = 1.611$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 20111 reflections

$\theta = 3.3\text{--}30.1^\circ$

$\mu = 0.43$ mm⁻¹

$T = 120$ K

Block, brown

$0.39 \times 0.36 \times 0.21$ mm

Data collection

Rigaku R-AXIS RAPIDII

diffractometer

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

$T_{\min} = 0.804$, $T_{\max} = 0.913$

22767 measured reflections

2401 independent reflections

2316 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -16 \rightarrow 16$

$k = -4 \rightarrow 5$

$l = -30 \rightarrow 30$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.076$

$S = 1.06$

2401 reflections

124 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.3557P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.60869 (2)	0.78653 (6)	0.40403 (2)	0.01704 (8)
O1	0.33921 (7)	0.8229 (2)	0.37552 (4)	0.02149 (16)
O2	0.75999 (6)	0.4050 (2)	0.54453 (4)	0.01794 (15)
H2	0.8039 (15)	0.289 (4)	0.5870 (8)	0.027*
O3	0.92219 (7)	0.1199 (2)	0.66164 (4)	0.02094 (16)
N1	1.13199 (8)	-0.0736 (2)	0.72858 (4)	0.01604 (16)
H1	1.1281 (13)	-0.016 (4)	0.7672 (8)	0.024*
C1	0.41591 (9)	0.6765 (2)	0.43248 (5)	0.01361 (17)
C2	0.55361 (8)	0.6274 (3)	0.45806 (5)	0.01311 (16)
C3	0.63639 (8)	0.4587 (2)	0.52136 (5)	0.01342 (17)
C4	1.02174 (9)	-0.0153 (3)	0.66317 (5)	0.01563 (17)
C5	1.02800 (9)	-0.1116 (3)	0.60168 (5)	0.01779 (18)
H5	0.953363	-0.080221	0.554948	0.021*
C6	1.14171 (10)	-0.2497 (3)	0.60990 (5)	0.01837 (19)
H6	1.145376	-0.312374	0.568705	0.022*
C7	1.25330 (10)	-0.2995 (3)	0.67902 (5)	0.01870 (19)
H7	1.332337	-0.392760	0.684778	0.022*
C8	1.24515 (9)	-0.2109 (3)	0.73732 (5)	0.01775 (18)
H8	1.318846	-0.245048	0.784277	0.021*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02123 (12)	0.01778 (12)	0.01883 (12)	0.00121 (8)	0.01512 (10)	0.00259 (7)
O1	0.0172 (3)	0.0304 (4)	0.0166 (3)	0.0046 (3)	0.0086 (3)	0.0080 (3)
O2	0.0124 (3)	0.0244 (4)	0.0172 (3)	0.0022 (3)	0.0079 (2)	0.0040 (3)
O3	0.0149 (3)	0.0307 (4)	0.0184 (3)	0.0048 (3)	0.0095 (3)	0.0034 (3)
N1	0.0158 (3)	0.0189 (4)	0.0145 (3)	0.0021 (3)	0.0086 (3)	0.0000 (3)
C1	0.0150 (4)	0.0138 (4)	0.0134 (4)	0.0000 (3)	0.0083 (3)	-0.0005 (3)
C2	0.0150 (4)	0.0139 (4)	0.0139 (4)	0.0000 (3)	0.0098 (3)	0.0002 (3)
C3	0.0139 (4)	0.0137 (4)	0.0143 (4)	-0.0005 (3)	0.0084 (3)	-0.0010 (3)
C4	0.0142 (4)	0.0170 (4)	0.0162 (4)	-0.0005 (3)	0.0083 (3)	0.0012 (3)
C5	0.0178 (4)	0.0207 (4)	0.0146 (4)	-0.0011 (3)	0.0082 (3)	0.0004 (3)
C6	0.0221 (4)	0.0189 (4)	0.0179 (4)	-0.0015 (3)	0.0131 (4)	-0.0018 (3)
C7	0.0184 (4)	0.0190 (4)	0.0211 (4)	0.0023 (3)	0.0119 (4)	-0.0009 (3)
C8	0.0157 (4)	0.0191 (4)	0.0174 (4)	0.0033 (3)	0.0078 (3)	0.0002 (3)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.7233 (9)	C2—C3	1.3614 (12)
O1—C1	1.2217 (11)	C4—C5	1.4256 (13)
O2—C3	1.3033 (10)	C5—C6	1.3726 (14)
O2—H2	0.901 (16)	C5—H5	0.9500
O3—C4	1.2739 (11)	C6—C7	1.4120 (14)
N1—C8	1.3611 (12)	C6—H6	0.9500
N1—C4	1.3648 (11)	C7—C8	1.3636 (14)
N1—H1	0.892 (15)	C7—H7	0.9500
C1—C2	1.4475 (12)	C8—H8	0.9500
C1—C3 ⁱ	1.5182 (12)		
C3—O2—H2	114.1 (10)	O3—C4—C5	125.24 (8)
C8—N1—C4	123.66 (8)	N1—C4—C5	116.69 (8)
C8—N1—H1	119.5 (9)	C6—C5—C4	120.10 (9)
C4—N1—H1	116.9 (9)	C6—C5—H5	120.0
O1—C1—C2	123.32 (8)	C4—C5—H5	120.0
O1—C1—C3 ⁱ	118.05 (8)	C5—C6—C7	120.62 (9)
C2—C1—C3 ⁱ	118.63 (7)	C5—C6—H6	119.7
C3—C2—C1	121.99 (8)	C7—C6—H6	119.7
C3—C2—C11	121.00 (7)	C8—C7—C6	118.57 (9)
C1—C2—C11	117.01 (7)	C8—C7—H7	120.7
O2—C3—C2	122.88 (8)	C6—C7—H7	120.7
O2—C3—C1 ⁱ	117.75 (8)	N1—C8—C7	120.35 (9)
C2—C3—C1 ⁱ	119.37 (8)	N1—C8—H8	119.8
O3—C4—N1	118.06 (8)	C7—C8—H8	119.8
O1—C1—C2—C3	-179.08 (9)	C8—N1—C4—O3	-178.90 (9)
C3 ⁱ —C1—C2—C3	1.18 (15)	C8—N1—C4—C5	1.04 (15)
O1—C1—C2—C11	-0.05 (13)	O3—C4—C5—C6	178.84 (10)
C3 ⁱ —C1—C2—C11	-179.79 (6)	N1—C4—C5—C6	-1.09 (15)
C1—C2—C3—O2	178.46 (9)	C4—C5—C6—C7	0.28 (16)
C11—C2—C3—O2	-0.53 (14)	C5—C6—C7—C8	0.64 (16)
C1—C2—C3—C1 ⁱ	-1.19 (15)	C4—N1—C8—C7	-0.13 (16)
C11—C2—C3—C1 ⁱ	179.82 (7)	C6—C7—C8—N1	-0.73 (15)

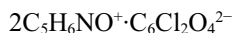
Symmetry code: (i) $-x+1, -y+1, -z+1$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O3	0.901 (15)	1.627 (16)	2.4989 (11)	161.9 (19)
N1—H1 \cdots O3 ⁱⁱ	0.893 (16)	1.996 (17)	2.8743 (12)	167.6 (16)
C7—H7 \cdots C11 ⁱⁱⁱ	0.95	2.79	3.5122 (13)	134

Symmetry codes: (ii) $-x+2, y, -z+3/2$; (iii) $-x+2, -y, -z+1$.

Bis(3-hydroxypyridinium) 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-diolate (II)

Crystal data

 $M_r = 399.19$ Monoclinic, $P2_1/c$ $a = 8.3659$ (6) Å $b = 8.5492$ (6) Å $c = 11.7087$ (8) Å $\beta = 106.968$ (3)° $V = 800.98$ (9) Å³ $Z = 2$ $F(000) = 408.00$ $D_x = 1.655$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 13386 reflections

 $\theta = 3.0$ – 30.0 ° $\mu = 0.45$ mm⁻¹ $T = 120$ K

Block, brown

 $0.21 \times 0.20 \times 0.12$ mm

Data collection

Rigaku R-AXIS RAPIDII

diffractometer

Detector resolution: 10.000 pixels mm⁻¹ ω scans

Absorption correction: numerical

(NUMABS; Higashi, 1999)

 $T_{\min} = 0.903$, $T_{\max} = 0.948$

15315 measured reflections

2329 independent reflections

2166 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.017$ $\theta_{\max} = 30.0$ °, $\theta_{\min} = 3.0$ ° $h = -11 \rightarrow 11$ $k = -12 \rightarrow 12$ $l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.028$ $wR(F^2) = 0.075$ $S = 1.07$

2329 reflections

124 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.357P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.52$ e Å⁻³ $\Delta\rho_{\min} = -0.20$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.93157 (3)	0.73912 (3)	0.68834 (2)	0.01680 (8)
O1	1.24731 (9)	0.58136 (9)	0.69329 (7)	0.01740 (16)
O2	0.68396 (9)	0.61601 (9)	0.46095 (7)	0.01689 (16)
O3	0.41012 (10)	0.51422 (9)	0.30475 (7)	0.01640 (16)
H3	0.509 (2)	0.5340 (19)	0.3482 (15)	0.025*
N1	0.48820 (11)	0.71217 (11)	0.05541 (8)	0.01529 (17)
H1	0.566 (2)	0.7718 (19)	0.0393 (15)	0.023*
C1	1.13017 (12)	0.54789 (11)	0.60534 (9)	0.01283 (18)
C2	0.96428 (12)	0.60823 (12)	0.58348 (9)	0.01358 (18)

C3	0.83396 (12)	0.56708 (12)	0.48551 (9)	0.01327 (18)
C4	0.51167 (12)	0.66180 (12)	0.16734 (9)	0.01383 (18)
H4	0.609229	0.691448	0.228545	0.017*
C5	0.39288 (12)	0.56593 (11)	0.19388 (9)	0.01309 (18)
C6	0.25163 (13)	0.52430 (13)	0.10152 (10)	0.0171 (2)
H6	0.169400	0.457667	0.116909	0.021*
C7	0.23181 (14)	0.58069 (13)	-0.01295 (10)	0.0192 (2)
H7	0.135178	0.553857	-0.075971	0.023*
C8	0.35290 (14)	0.67593 (13)	-0.03506 (9)	0.0180 (2)
H8	0.340534	0.715121	-0.113094	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01596 (13)	0.01889 (13)	0.01530 (13)	0.00248 (8)	0.00420 (9)	-0.00478 (8)
O1	0.0143 (3)	0.0210 (4)	0.0144 (3)	0.0017 (3)	0.0004 (3)	-0.0030 (3)
O2	0.0118 (3)	0.0224 (4)	0.0151 (3)	0.0047 (3)	0.0018 (3)	-0.0023 (3)
O3	0.0141 (3)	0.0203 (4)	0.0142 (3)	-0.0010 (3)	0.0032 (3)	0.0034 (3)
N1	0.0148 (4)	0.0160 (4)	0.0155 (4)	-0.0020 (3)	0.0050 (3)	0.0005 (3)
C1	0.0129 (4)	0.0133 (4)	0.0121 (4)	0.0010 (3)	0.0034 (3)	0.0006 (3)
C2	0.0134 (4)	0.0151 (4)	0.0122 (4)	0.0021 (3)	0.0036 (3)	-0.0021 (3)
C3	0.0132 (4)	0.0144 (4)	0.0120 (4)	0.0016 (3)	0.0034 (3)	0.0006 (3)
C4	0.0122 (4)	0.0142 (4)	0.0142 (4)	-0.0007 (3)	0.0025 (3)	0.0001 (3)
C5	0.0121 (4)	0.0127 (4)	0.0144 (4)	0.0010 (3)	0.0037 (3)	0.0001 (3)
C6	0.0129 (4)	0.0180 (5)	0.0194 (5)	-0.0033 (3)	0.0031 (4)	0.0000 (4)
C7	0.0167 (5)	0.0209 (5)	0.0169 (5)	-0.0031 (4)	-0.0001 (4)	-0.0019 (4)
C8	0.0198 (5)	0.0199 (5)	0.0132 (4)	-0.0014 (4)	0.0031 (4)	-0.0005 (4)

Geometric parameters (Å, °)

Cl1—C2	1.7409 (10)	C2—C3	1.3778 (13)
O1—C1	1.2302 (12)	C4—C5	1.3915 (13)
O2—C3	1.2735 (12)	C4—H4	0.9500
O3—C5	1.3387 (12)	C5—C6	1.3952 (14)
O3—H3	0.850 (18)	C6—C7	1.3880 (15)
N1—C4	1.3384 (13)	C6—H6	0.9500
N1—C8	1.3414 (14)	C7—C8	1.3818 (15)
N1—H1	0.891 (17)	C7—H7	0.9500
C1—C2	1.4319 (13)	C8—H8	0.9500
C1—C3 ⁱ	1.5409 (14)		
C5—O3—H3	109.0 (11)	N1—C4—H4	120.1
C4—N1—C8	123.22 (9)	C5—C4—H4	120.1
C4—N1—H1	119.0 (11)	O3—C5—C4	121.95 (9)
C8—N1—H1	117.8 (11)	O3—C5—C6	119.64 (9)
O1—C1—C2	124.03 (9)	C4—C5—C6	118.41 (9)
O1—C1—C3 ⁱ	117.27 (8)	C7—C6—C5	119.69 (9)
C2—C1—C3 ⁱ	118.70 (8)	C7—C6—H6	120.2

C3—C2—C1	123.17 (9)	C5—C6—H6	120.2
C3—C2—Cl1	120.15 (7)	C8—C7—C6	119.88 (9)
C1—C2—Cl1	116.69 (7)	C8—C7—H7	120.1
O2—C3—C2	126.33 (9)	C6—C7—H7	120.1
O2—C3—C1 ⁱ	115.54 (8)	N1—C8—C7	118.94 (9)
C2—C3—C1 ⁱ	118.13 (8)	N1—C8—H8	120.5
N1—C4—C5	119.86 (9)	C7—C8—H8	120.5
O1—C1—C2—C3	-178.76 (10)	C8—N1—C4—C5	0.55 (16)
C3 ⁱ —C1—C2—C3	0.78 (16)	N1—C4—C5—O3	-179.23 (9)
O1—C1—C2—Cl1	1.08 (14)	N1—C4—C5—C6	0.30 (15)
C3 ⁱ —C1—C2—Cl1	-179.38 (7)	O3—C5—C6—C7	178.57 (10)
C1—C2—C3—O2	179.87 (10)	C4—C5—C6—C7	-0.97 (15)
Cl1—C2—C3—O2	0.03 (15)	C5—C6—C7—C8	0.83 (17)
C1—C2—C3—C1 ⁱ	-0.78 (16)	C4—N1—C8—C7	-0.70 (16)
Cl1—C2—C3—C1 ⁱ	179.39 (7)	C6—C7—C8—N1	-0.01 (17)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O2	0.852 (17)	1.803 (17)	2.6277 (12)	162.5 (16)
O3—H3 \cdots O1 ⁱ	0.852 (17)	2.438 (17)	2.9738 (12)	121.6 (14)
N1—H1 \cdots O2 ⁱⁱ	0.889 (17)	1.807 (17)	2.6684 (12)	162.6 (16)
C8—H8 \cdots O1 ⁱⁱⁱ	0.95	2.45	3.1481 (13)	130

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x, -y+3/2, z-1/2$; (iii) $x-1, y, z-1$.

Bis(4-hydroxypyridinium) 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-diolate (III)

Crystal data

$2\text{C}_5\text{H}_6\text{NO}^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}$

$M_r = 399.19$

Triclinic, $P\bar{1}$

$a = 5.49136$ (13) \AA

$b = 8.2195$ (4) \AA

$c = 18.1382$ (9) \AA

$\alpha = 102.177$ (3) $^\circ$

$\beta = 93.952$ (3) $^\circ$

$\gamma = 95.316$ (4) $^\circ$

$V = 793.52$ (6) \AA^3

$Z = 2$

$F(000) = 408.00$

$D_x = 1.671$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71075$ \AA

Cell parameters from 11077 reflections

$\theta = 3.0\text{--}30.1^\circ$

$\mu = 0.45$ mm^{-1}

$T = 120$ K

Platelet, brown

$0.35 \times 0.25 \times 0.12$ mm

Data collection

Rigaku R-AXIS RAPIDII

diffractometer

Detector resolution: 10.000 pixels mm^{-1}

ω scans

Absorption correction: numerical

(NUMABS; Higashi, 1999)

$T_{\min} = 0.890$, $T_{\max} = 0.948$

12373 measured reflections

4597 independent reflections

4124 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -7 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.080$

$S = 1.07$

4597 reflections

247 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.3136P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.42856 (5)	0.16233 (3)	-0.07860 (2)	0.01668 (7)
Cl2	1.13911 (5)	0.28348 (3)	0.52483 (2)	0.01730 (7)
O1	0.03685 (16)	-0.10701 (11)	-0.14946 (5)	0.02014 (18)
O2	0.33010 (15)	0.24516 (10)	0.08473 (5)	0.01729 (17)
O3	1.55337 (16)	0.23416 (11)	0.62981 (5)	0.01865 (17)
O4	1.14201 (15)	0.00027 (10)	0.38854 (5)	0.01586 (16)
O5	0.18017 (16)	0.33437 (10)	0.25526 (5)	0.01818 (17)
H5	0.118 (3)	0.263 (2)	0.2115 (10)	0.027*
O6	0.74923 (17)	0.40347 (11)	0.05992 (5)	0.02044 (18)
H6	0.617 (3)	0.350 (2)	0.0681 (11)	0.031*
N1	0.76255 (18)	0.16991 (12)	0.35832 (6)	0.01695 (19)
H1	0.896 (3)	0.128 (2)	0.3779 (10)	0.025*
N2	1.04584 (18)	0.71260 (12)	0.25721 (6)	0.01696 (19)
H2	1.114 (3)	0.777 (2)	0.2998 (10)	0.025*
C1	0.02618 (19)	-0.05358 (13)	-0.08002 (6)	0.01355 (19)
C2	0.19204 (19)	0.07509 (13)	-0.03554 (6)	0.01332 (19)
C3	0.18242 (19)	0.13365 (13)	0.04220 (6)	0.01289 (19)
C4	1.52060 (19)	0.12916 (13)	0.56903 (6)	0.01293 (19)
C5	1.33437 (19)	0.12624 (13)	0.51055 (6)	0.01346 (19)
C6	1.30221 (19)	0.00728 (13)	0.44252 (6)	0.01271 (19)
C7	0.6571 (2)	0.30150 (14)	0.39505 (7)	0.0178 (2)
H7	0.719110	0.355184	0.445342	0.021*
C8	0.4617 (2)	0.35945 (14)	0.36116 (7)	0.0169 (2)
H8	0.390102	0.453256	0.387366	0.020*
C9	0.3693 (2)	0.27801 (13)	0.28719 (6)	0.0141 (2)
C10	0.4863 (2)	0.14337 (14)	0.24949 (6)	0.0169 (2)
H10	0.430463	0.088006	0.198898	0.020*
C11	0.6819 (2)	0.09297 (15)	0.28659 (7)	0.0180 (2)

H11	0.761693	0.002289	0.261273	0.022*
C12	0.8247 (2)	0.62477 (14)	0.25631 (6)	0.0169 (2)
H12	0.743357	0.635815	0.301370	0.020*
C13	0.7170 (2)	0.51997 (14)	0.19096 (6)	0.0152 (2)
H13	0.560916	0.459117	0.190415	0.018*
C14	0.8392 (2)	0.50334 (13)	0.12492 (6)	0.0145 (2)
C15	1.0695 (2)	0.59750 (15)	0.12741 (7)	0.0178 (2)
H15	1.155223	0.590054	0.083294	0.021*
C16	1.1663 (2)	0.69955 (15)	0.19462 (7)	0.0181 (2)
H16	1.321913	0.762460	0.197088	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01602 (12)	0.01837 (13)	0.01388 (12)	−0.00454 (9)	0.00310 (9)	0.00181 (9)
Cl2	0.01776 (13)	0.01555 (12)	0.01668 (13)	0.00527 (9)	−0.00194 (9)	−0.00109 (9)
O1	0.0204 (4)	0.0252 (4)	0.0108 (4)	−0.0062 (3)	0.0022 (3)	−0.0016 (3)
O2	0.0165 (4)	0.0179 (4)	0.0136 (4)	−0.0054 (3)	−0.0007 (3)	−0.0014 (3)
O3	0.0202 (4)	0.0181 (4)	0.0140 (4)	0.0038 (3)	−0.0031 (3)	−0.0038 (3)
O4	0.0164 (4)	0.0164 (4)	0.0129 (4)	0.0021 (3)	−0.0034 (3)	0.0005 (3)
O5	0.0183 (4)	0.0175 (4)	0.0162 (4)	0.0037 (3)	−0.0050 (3)	−0.0004 (3)
O6	0.0196 (4)	0.0230 (4)	0.0135 (4)	−0.0083 (3)	0.0008 (3)	−0.0029 (3)
N1	0.0157 (4)	0.0177 (4)	0.0181 (5)	0.0022 (3)	−0.0003 (4)	0.0057 (4)
N2	0.0177 (4)	0.0173 (4)	0.0128 (4)	−0.0016 (3)	−0.0028 (4)	−0.0006 (3)
C1	0.0126 (4)	0.0151 (5)	0.0117 (5)	−0.0008 (4)	0.0003 (4)	0.0014 (4)
C2	0.0118 (4)	0.0151 (4)	0.0121 (5)	−0.0025 (4)	0.0018 (4)	0.0023 (4)
C3	0.0120 (4)	0.0131 (4)	0.0126 (5)	−0.0004 (3)	0.0000 (4)	0.0019 (4)
C4	0.0134 (4)	0.0129 (4)	0.0116 (5)	0.0001 (4)	0.0011 (4)	0.0012 (4)
C5	0.0135 (4)	0.0128 (4)	0.0133 (5)	0.0028 (4)	−0.0001 (4)	0.0007 (4)
C6	0.0122 (4)	0.0124 (4)	0.0126 (5)	−0.0005 (3)	−0.0001 (4)	0.0020 (4)
C7	0.0200 (5)	0.0153 (5)	0.0162 (5)	0.0000 (4)	−0.0032 (4)	0.0016 (4)
C8	0.0196 (5)	0.0141 (5)	0.0154 (5)	0.0020 (4)	−0.0011 (4)	0.0003 (4)
C9	0.0144 (4)	0.0131 (4)	0.0146 (5)	0.0000 (4)	0.0006 (4)	0.0032 (4)
C10	0.0201 (5)	0.0171 (5)	0.0125 (5)	0.0027 (4)	0.0010 (4)	0.0012 (4)
C11	0.0197 (5)	0.0180 (5)	0.0170 (5)	0.0045 (4)	0.0043 (4)	0.0034 (4)
C12	0.0170 (5)	0.0198 (5)	0.0129 (5)	0.0010 (4)	0.0016 (4)	0.0015 (4)
C13	0.0132 (4)	0.0164 (5)	0.0147 (5)	−0.0011 (4)	0.0008 (4)	0.0019 (4)
C14	0.0149 (5)	0.0137 (4)	0.0129 (5)	−0.0006 (4)	−0.0006 (4)	0.0002 (4)
C15	0.0156 (5)	0.0205 (5)	0.0148 (5)	−0.0039 (4)	0.0023 (4)	0.0001 (4)
C16	0.0146 (5)	0.0191 (5)	0.0181 (5)	−0.0032 (4)	−0.0001 (4)	0.0010 (4)

Geometric parameters (Å, °)

Cl1—C2	1.7363 (11)	C4—C5	1.4165 (14)
Cl2—C5	1.7438 (11)	C4—C6 ⁱⁱ	1.5426 (15)
O1—C1	1.2508 (13)	C5—C6	1.3924 (15)
O2—C3	1.2532 (12)	C7—C8	1.3722 (16)
O3—C4	1.2390 (13)	C7—H7	0.9500

O4—C6	1.2586 (13)	C8—C9	1.4035 (15)
O5—C9	1.3223 (13)	C8—H8	0.9500
O5—H5	0.907 (18)	C9—C10	1.4065 (16)
O6—C14	1.3208 (13)	C10—C11	1.3703 (16)
O6—H6	0.852 (19)	C10—H10	0.9500
N1—C11	1.3456 (15)	C11—H11	0.9500
N1—C7	1.3469 (15)	C12—C13	1.3693 (15)
N1—H1	0.918 (18)	C12—H12	0.9500
N2—C16	1.3430 (16)	C13—C14	1.4009 (16)
N2—C12	1.3511 (15)	C13—H13	0.9500
N2—H2	0.877 (18)	C14—C15	1.4126 (15)
C1—C2	1.3997 (14)	C15—C16	1.3671 (15)
C1—C3 ⁱ	1.5410 (15)	C15—H15	0.9500
C2—C3	1.3970 (15)	C16—H16	0.9500
C9—O5—H5	111.3 (11)	C8—C7—H7	119.4
C14—O6—H6	107.1 (13)	C7—C8—C9	118.99 (11)
C11—N1—C7	120.85 (10)	C7—C8—H8	120.5
C11—N1—H1	114.5 (11)	C9—C8—H8	120.5
C7—N1—H1	124.6 (11)	O5—C9—C8	118.46 (10)
C16—N2—C12	121.30 (10)	O5—C9—C10	122.89 (10)
C16—N2—H2	119.3 (12)	C8—C9—C10	118.62 (10)
C12—N2—H2	119.4 (12)	C11—C10—C9	119.23 (10)
O1—C1—C2	123.43 (10)	C11—C10—H10	120.4
O1—C1—C3 ⁱ	117.79 (9)	C9—C10—H10	120.4
C2—C1—C3 ⁱ	118.79 (9)	N1—C11—C10	121.03 (11)
C3—C2—C1	123.56 (10)	N1—C11—H11	119.5
C3—C2—C11	118.10 (8)	C10—C11—H11	119.5
C1—C2—C11	118.31 (8)	N2—C12—C13	120.52 (11)
O2—C3—C2	125.93 (10)	N2—C12—H12	119.7
O2—C3—C1 ⁱ	116.43 (9)	C13—C12—H12	119.7
C2—C3—C1 ⁱ	117.64 (9)	C12—C13—C14	119.37 (10)
O3—C4—C5	124.83 (10)	C12—C13—H13	120.3
O3—C4—C6 ⁱⁱ	116.58 (9)	C14—C13—H13	120.3
C5—C4—C6 ⁱⁱ	118.59 (9)	O6—C14—C13	123.08 (10)
C6—C5—C4	123.72 (10)	O6—C14—C15	118.05 (10)
C6—C5—C12	118.75 (8)	C13—C14—C15	118.87 (10)
C4—C5—C12	117.52 (8)	C16—C15—C14	118.63 (11)
O4—C6—C5	126.22 (10)	C16—C15—H15	120.7
O4—C6—C4 ⁱⁱ	116.09 (9)	C14—C15—H15	120.7
C5—C6—C4 ⁱⁱ	117.69 (9)	N2—C16—C15	121.29 (10)
N1—C7—C8	121.23 (11)	N2—C16—H16	119.4
N1—C7—H7	119.4	C15—C16—H16	119.4
O1—C1—C2—C3	-179.19 (11)	C11—N1—C7—C8	1.17 (18)
C3 ⁱ —C1—C2—C3	1.29 (18)	N1—C7—C8—C9	0.81 (18)
O1—C1—C2—C11	-1.30 (16)	C7—C8—C9—O5	179.64 (10)
C3 ⁱ —C1—C2—C11	179.17 (7)	C7—C8—C9—C10	-2.23 (17)

C1—C2—C3—O2	178.00 (11)	O5—C9—C10—C11	179.80 (10)
C11—C2—C3—O2	0.11 (16)	C8—C9—C10—C11	1.75 (17)
C1—C2—C3—C1 ⁱ	-1.27 (17)	C7—N1—C11—C10	-1.68 (17)
C11—C2—C3—C1 ⁱ	-179.16 (7)	C9—C10—C11—N1	0.18 (17)
O3—C4—C5—C6	179.64 (11)	C16—N2—C12—C13	-0.23 (17)
C6 ⁱⁱ —C4—C5—C6	-0.41 (17)	N2—C12—C13—C14	0.54 (17)
O3—C4—C5—C12	0.75 (16)	C12—C13—C14—O6	179.17 (11)
C6 ⁱⁱ —C4—C5—C12	-179.29 (7)	C12—C13—C14—C15	-0.92 (17)
C4—C5—C6—O4	-179.11 (10)	O6—C14—C15—C16	-179.08 (11)
C12—C5—C6—O4	-0.23 (16)	C13—C14—C15—C16	1.01 (17)
C4—C5—C6—C4 ⁱⁱ	0.40 (17)	C12—N2—C16—C15	0.33 (18)
C12—C5—C6—C4 ⁱⁱ	179.28 (7)	C14—C15—C16—N2	-0.72 (18)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x+3, -y, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O1 ⁱ	0.905 (17)	1.640 (17)	2.5208 (13)	163.2 (17)
O6—H6 \cdots O2	0.852 (17)	1.800 (17)	2.6510 (13)	177.3 (18)
N1—H1 \cdots O4	0.919 (17)	1.810 (17)	2.7000 (13)	162.3 (16)
N2—H2 \cdots O4 ⁱⁱⁱ	0.876 (18)	2.156 (17)	2.9603 (14)	152.3 (15)
N2—H2 \cdots O3 ^{iv}	0.876 (18)	2.176 (17)	2.8384 (14)	132.1 (14)
C7—H7 \cdots C12	0.95	2.81	3.4540 (12)	126
C12—H12 \cdots O3 ^v	0.95	2.32	3.1541 (14)	146
C13—H13 \cdots O2	0.95	2.49	3.1685 (14)	128
C16—H16 \cdots C11 ^{vi}	0.95	2.77	3.4427 (12)	128

Symmetry codes: (i) $-x, -y, -z$; (iii) $x, y+1, z$; (iv) $-x+3, -y+1, -z+1$; (v) $-x+2, -y+1, -z+1$; (vi) $-x+2, -y+1, -z$.