research communications

Crystal structures of two 1:2 dihydrate compounds of chloranilic acid with 2-carboxypyridine and 2-carboxyquinoline

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The crystal structure of the 1:2 dihydrate compound of chloranilic acid (systematic name: 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) with 2-carboxypyridine (another common name: picolinic acid; systematic name: pyr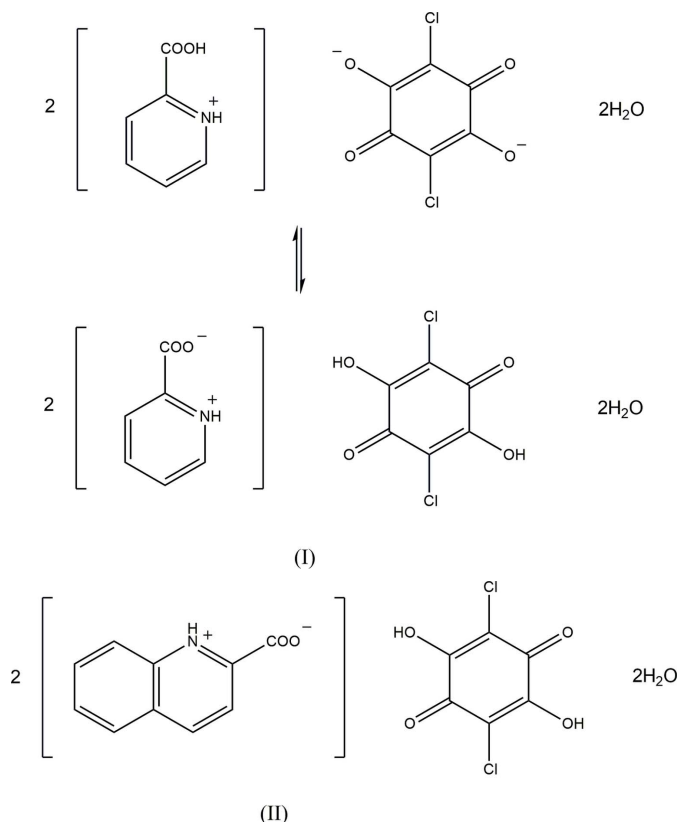idine-2-carboxylic acid), namely, $2C_6H_{5.5}NO_2^{0.5+}\cdot C_6HCl_2O_4^-\cdot 2H_2O$, (I), has been determined at 180 K, and the structure of the 1:2 dihydrate compound of chloranilic acid with 2-carboxyquinoline (another common name: quinaldic acid; systematic name: quinoline-2-carboxylic acid), namely, $2C_{10}H_7NO_2\cdot C_6H_2Cl_2O_4\cdot 2H_2O$, (II), has been redetermined at 200 K. This determination presents a higher precision crystal structure than the previously published structure [Marfo-Owusu & Thompson (2014). *X-ray Struct. Anal. Online*, **30**, 55–56]. Compound (I) was analysed as a disordered structure over two states, *viz.* salt and co-crystal. The salt is bis(2-carboxypyridinium) chloranilate dihydrate, $2C_6H_6NO_2^+\cdot C_6Cl_2O_4^{2-}\cdot 2H_2O$, and the co-crystal is bis(pyridinium-2-carboxylate) chloranilic acid dihydrate, $2C_6H_5NO_2\cdot C_6H_2Cl_2O_4\cdot 2H_2O$, including zwitterionic 2-carboxypyridine. In both salt and co-crystal, the water molecule links the chloranilic acid and 2-carboxypyridine molecules through O—H⋯O and N—H⋯O hydrogen bonds. The 2-carboxypyridine molecules are connected into a head-to-head inversion dimer by a short O—H⋯O hydrogen bond, in which the H atom is disordered over two positions. Compound (II) is a 1:2 dihydrate co-crystal of chloranilic acid and zwitterionic 2-carboxyquinoline. The water molecule links the chloranilic acid and 2-carboxyquinoline molecules through O—H⋯O hydrogen bonds. The 2-carboxyquinoline molecules are connected into a head-to-tail inversion dimer by a pair of N—H⋯O hydrogen bonds.

1. Chemical context

Chloranilic acid, a dibasic acid with hydrogen-bond donor as well as acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with various pyridine derivatives as well as being a model compound for investigating hydrogen-transfer motions in O—H⋯N and N—H⋯O hydrogen-bond systems (Zaman *et al.*, 2004; Molčanov & Kojić-Prodić, 2010; Seliger *et al.*, 2009; Asaji *et al.* 2010). Previously, we have prepared three 1:1 compounds of chloranilic acid with 2-, 3- and 4-carboxypyridine and analysed the crystal structures in order to extend our study on D—H⋯A hydrogen bonding (D = N, O or C; A = N, O or Cl) in chloranilic acid–substituted pyridine systems (Gotoh *et al.*, 2006, 2009; Tabuchi *et al.*, 2005). In the present study, we have prepared a 1:2 compound of chloranilic acid with 2-carboxypyridine and also redetermined the structure of a 1:2 compound of chloranilic acid with 2-carboxyquinoline with higher precision than previously reported structure [Marfo-
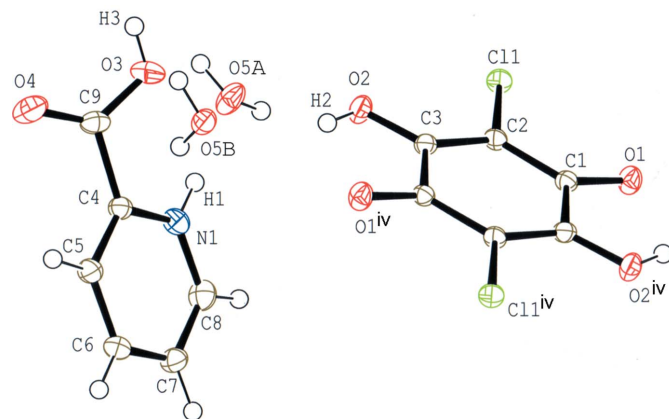

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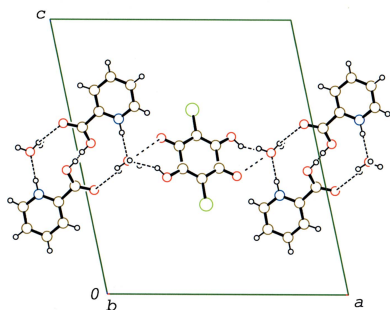
Owusu & Thompson, 2014; although the title and text in this reference refer to the 1:1 adduct of chloranilic acid with 2-carboxyqulinone, the reported structure is the 1:2 compound, the same as the present compound (II)]. The crystal structure of the anhydrous 1:2 compound of chloranilic acid with 2-carboxyquinoline was also reported by Marfo-Owusu & Thompson (2016).
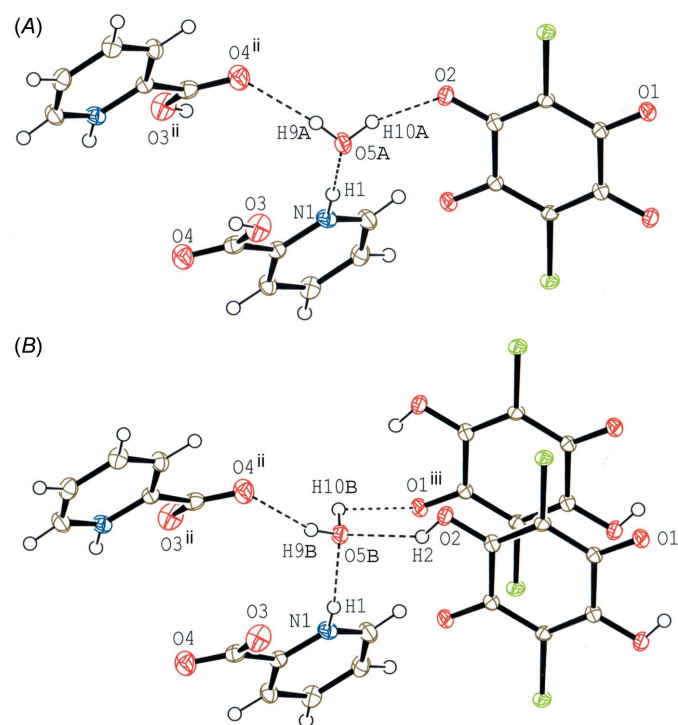

Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. The water molecule is disordered over two sites with equally occupancies. Atoms H2 and H3 have site-occupancy factors of 0.5. [Symmetry code: (iv) −x + 1, −y + 1, −z + 1.]

between the pyridine ring and the carboxy plane in the base molecule is 23.32 (15)°.

The asymmetric unit of compound (II) consists of one-half of a chloranilic acid molecule, which is located on an inversion centre, one 2-carboxyquinoline molecule and one water molecule. In the crystal, the 2-carboxyquinoline molecule is in a

2. Structural commentary

Compound (I) (Fig. 1) crystallizes with one-half of a chloranilic acid molecule, which is located on an inversion centre, one 2-carboxypyridine molecule and one water molecule in the asymmetric unit. In the crystal, the water molecule is disordered over two sites with equal occupancies of 0.5. The occupancies of the H atoms in the chloranilic acid molecule and the carboxy group of the 2-carboxypyridine molecule are also 0.5. The compound is, therefore, considered to be a disordered state over two forms, *viz.* bis(2-carboxypyridinium) chloranilate dihydrate, (*A*), and bis(pyridinium-2-carboxylate) chloranilic acid dihydrate, (*B*), as shown in the scheme and Fig. 2. In form (*A*), the water molecule acts as one N—H···O hydrogen-bond acceptor and two O—H···O hydrogen-bond donors (N1—H1···O5*A*, O5*A*—O9*A*···O4^{ii} and O5*A*—H10*A*···O2; symmetry code as in Table 1), while in form (*B*), the water molecule acts as the acceptor of N—H···O and O—H···O hydrogen bonds, and as two O—H···O hydrogen-bond donors (N1—H1···O5*B*, O2—H2···O5*B*, O5*B*—H9*B*···O4^{ii} and O5*B*—H10*B*···O1^{iii}; Table 1). The dihedral angle

Figure 2
A partial packing diagram of compound (I) around the disordered water molecule in bis(2-carboxypyridinium) chloranilate dihydrate (*A*) and bis(pyridinium-2-carboxylate) chloranilic acid dihydrate (*B*), showing O—H···O and N—H···O hydrogen bonds (dashed lines). [Symmetry codes: (ii) −x, −y, −z + 1; (iii) −x + 1, −y, −z + 1.]
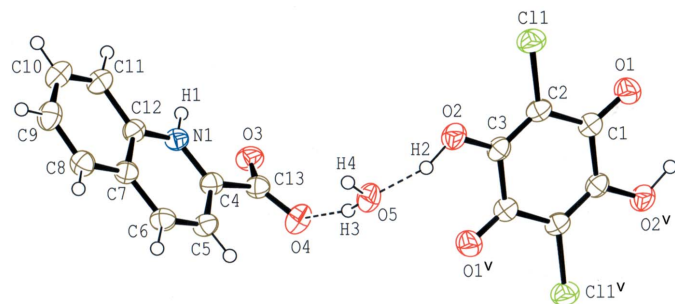
Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1$\cdots$O5A	0.895 (17)	1.843 (17)	2.7380 (19)	179 (2)
N1—H1$\cdots$O5B	0.895 (17)	1.907 (17)	2.7417 (18)	154 (2)
O2—H2$\cdots$O5B	0.83 (3)	2.12 (3)	2.8111 (19)	141 (3)
O3—H3$\cdots$O3^i	0.82 (3)	1.62 (4)	2.4352 (14)	174 (4)
O5A—H9A$\cdots$O4^{ii}	0.82 (3)	2.11 (3)	2.927 (2)	170 (3)
O5B—H9B$\cdots$O4^{ii}	0.82 (3)	2.02 (3)	2.8159 (19)	162 (3)
O5A—H10A$\cdots$O2	0.84 (3)	1.90 (3)	2.6762 (19)	154 (4)
O5B—H10B$\cdots$O1^{iii}	0.85 (2)	2.60 (3)	3.095 (2)	119 (2)
C8—H8$\cdots$Cl1^{iii}	0.95	2.78	3.6524 (12)	154
C8—H8$\cdots$O1^{iii}	0.95	2.47	3.1871 (14)	132

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1$\cdots$O3^i	0.88 (2)	1.91 (2)	2.7724 (17)	167 (2)
O2—H2$\cdots$O5	0.98 (3)	1.59 (3)	2.5092 (17)	155 (3)
O5—H3$\cdots$O4	0.82 (2)	2.01 (2)	2.8072 (19)	164 (2)
O5—H4$\cdots$O4^{ii}	0.85 (2)	1.82 (2)	2.6632 (19)	171 (2)
C6—H6$\cdots$O1^{iii}	0.95	2.54	3.392 (2)	150
C6—H6$\cdots$O5^{iv}	0.95	2.47	3.211 (2)	134

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

twitterionic form and no acid–base interaction involving H-atom transfer between chloranilic acid and 2-carboxyquinoline is observed (Fig. 3). The dihedral angle between the quinoline ring system and the carboxylate plane in the base molecule is 20.84 (19)°. The water molecule acts as an O—H$\cdots$O hydrogen-bonding bridge between the chloranilic and 2-carboxyquinoline molecules (O2—H2$\cdots$O5 and O5—H3$\cdots$O4; Table 2).

3. Supramolecular features

In the crystal of compound (I), the 2-carboxypyridine molecules, which are related by an inversion centre, are linked into a head-to-head dimer *via* a short O—H$\cdots$O hydrogen bond, in which the H atom is disordered over two sites (O3—H3$\cdots$O3^i; Table 1), as observed in pyridinium-2-carboxylic acid pyridinium-2-carboxylate perchlorate (Wang *et al.*, 2015). The three components are linked *via* the above-mentioned O—H$\cdots$O and N—H$\cdots$O hydrogen bonds together with weak C—H$\cdots$Cl and C—H$\cdots$O hydrogen bonds (C8—H8$\cdots$Cl1^{iii} and C8—H8$\cdots$O1^{iii}; Table 1), forming a layer parallel to the *ab* plane (Fig. 4). In the layer, the chloranilic acid rings are stacked along the *b* axis through a π–π interaction [centroid–centroid distance = 3.6851 (7) Å and interplanar spacing = 3.2118 (4) Å]. The pyridine rings are also

stacked along the *b* axis through a π–π interaction [centroid–centroid distance = 3.6851 (7) Å and interplanar spacing = 3.4787 (5) Å]. Between the layers, a short Cl$\cdots$Cl contact is observed [Cl1$\cdots$Cl1^v = 3.3717 (5) Å; symmetry code: (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$].

In the crystal of (II), two adjacent 2-carboxyquinoline molecules, which are related by an inversion centre, form a head-to-tail dimer *via* a pair of N—H$\cdots$O hydrogen bonds (N—H1$\cdots$O3^i; symmetry code as in Table 2). The dimers are stacked in a column along the *a* axis through a weak π–π interaction between the N1/C4–C7/C12 and C7–C12 rings with a centroid–centroid distance of 3.9184 (10) Å. The water molecule links the stacked base molecules related by translation along *a via* O—H$\cdots$O hydrogen bonds [O5—H3$\cdots$O4 and O5—H4$\cdots$O4^{ii}; Table 2] and also links the acid molecule and the two base molecules *via* O—H$\cdots$O hydrogen bonds, forming a layer structure parallel to (0$\bar{1}$1) as shown in Fig. 5. No significant short contact between the acid molecules in the layer is observed. Between the layers, a bifurcated C—H$\cdots$(O, O) hydrogen bond (C6—H6$\cdots$O1^{iii} and C6—H6$\cdots$O5^{iv}; Table 2) is observed, through which the 2-carboxyquinoline molecule is weakly linked with the chloranilic acid and water molecules.

Figure 3
The molecular structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. O—H$\cdots$O hydrogen bonds are shown as dashed lines. [Symmetry code: (v) $-x, -y, -z$.]
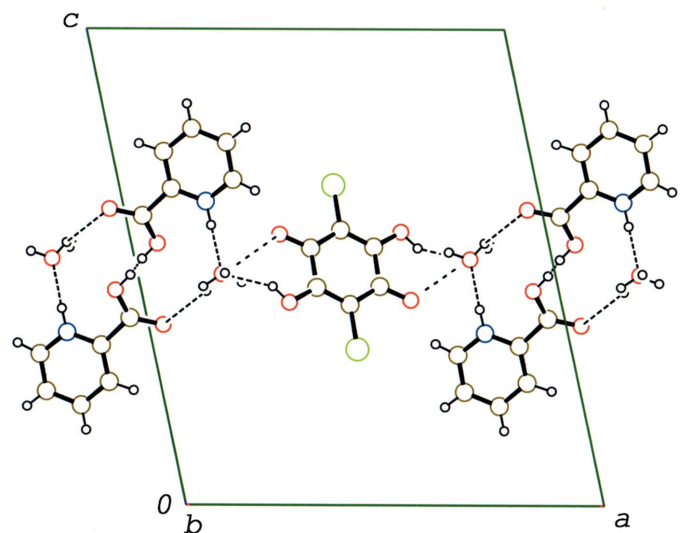

Figure 4
A packing diagram of compound (I) viewed along the *b* axis, showing the layer structure. O—H$\cdots$O and N—H$\cdots$O hydrogen bonds are shown as dashed lines.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$2C_6H_{5.5}NO_2{}^{0.5+}{\cdot}C_6HCl_2O_4{}^-{\cdot}2H_2O$	$2C_{10}H_7NO_2{\cdot}C_6H_2Cl_2O_4{\cdot}2H_2O$
M_r	491.24	591.36
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	180	200
a, b, c (Å)	15.1028 (10), 3.6851 (3), 17.5689 (13)	4.4745 (2), 10.5448 (8), 13.6111 (6)
α, β, γ (°)	90, 101.871 (3), 90	96.652 (4), 94.109 (3), 99.009 (4)
V (Å^3)	956.89 (12)	627.38 (6)
Z	2	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.40	0.32
Crystal size (mm)	$0.35 \times 0.18 \times 0.13$	$0.41 \times 0.21 \times 0.03$
Data collection		
Diffractometer	Rigaku R-AXIS RAPIDII	Rigaku R-AXIS RAPIDII
Absorption correction	Numerical (*NUMABS*; Higashi, 1999)	Numerical (*NUMABS*; Higashi, 1999)
T_{min}, T_{max}	0.896, 0.949	0.925, 0.990
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17752, 2789, 2537	12358, 3666, 2755
R_{int}	0.021	0.122
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.704	0.704
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.079, 1.11	0.052, 0.149, 1.01
No. of reflections	2789	3666
No. of parameters	176	197
No. of restraints	8	2
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
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.54, −0.24	0.52, −0.45

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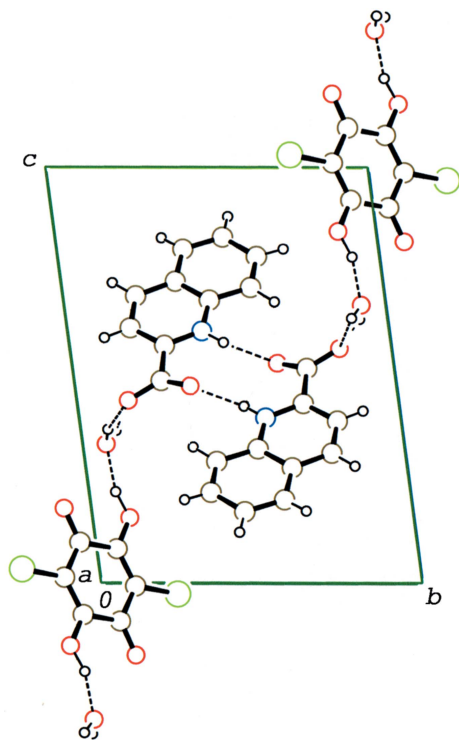

Figure 5
A packing diagram of compound (II) viewed along the *a* axis, showing the layer structure formed by O—H⋯O and N—H⋯O hydrogen bonds (dashed lines).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, last update May 2017; Groom *et al.*, 2016) for organic co-crystals of pyridinium-2-carboxylate (twitterionic form) gave six structures. For organic co-crystals of quinolinium-2-carboxylate (twitterionic form), eight structures were found.

5. Synthesis and crystallization

Single crystals of compound (I) were obtained by slow evaporation of an acetonitrile solution (200 ml) of chloranilic acid (250 mg) with 2-carboxypridine (310 mg) at room temperature. Single crystals of compound (II) were obtained by slow evaporation from a methanol solution (150 ml) of chloranilic acid (310 mg) with 2-carboxyquinoline (520 mg) at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The water molecule in compound (I) was found to be disordered over two sites in a difference-Fourier map. The occupancies were refined to 0.52 (2) and 0.48 (2) and then they were fixed at 0.5. The H atom in the carboxy group of the base molecule was also found in a

difference-Fourier map to be disordered between the adjacent carboxy groups, which are related by an inversion centre, and the occupancy was set to be 0.5. Since the N-bound H atom refined reasonably with an occupancy of 1, the occupancy of the H atom of the acid molecule was set to be 0.5 to balance the total charge of the compound. All other H atoms were found in a difference-Fourier map. The N-bound H atom was refined freely, while the positions of O-bound H atoms were refined, with O—H = 0.84 (2) Å and $U_{iso}(H) = 1.5U_{eq}(O)$. For the water H atoms, distant restraints of H$\cdots$H = 1.37 (4) Å were also applied. C-bound H atoms were positioned geometrically (C—H = 0.95 Å) and were treated as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

All H atoms in compound (II) were found in a difference-Fourier map. The O- and N-bound H atoms in the acid and base molecules were refined freely. The water H atoms were refined with O—H = 0.84 (2) Å. C-bound H atoms were positioned geometrically (C—H = 0.95 Å) and were treated as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

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supporting information

Crystal structures of two 1:2 dihydrate compounds of chloranilic acid with 2-carboxypyridine and 2-carboxyquinoline

Kazuma Gotoh and Hiroyuki Ishida

Computing details

For both 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) and *PLATON* (Spek, 2015).

Bis(2-carboxypyridinium) chloranilate dihydrate–bis(pyridinium-2-carboxylate) chloranilic acid dihydrate (1/1) (I)

Crystal data

$2C_6H_{5.5}NO_2 0.5+·C_6HCl_2O_4^-·2H_2O$	$F(000) = 504.00$
$M_r = 491.24$	$D_x = 1.705$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
$a = 15.1028$ (10) Å	Cell parameters from 15838 reflections
$b = 3.6851$ (3) Å	$\theta = 3.2$–$30.0°$
$c = 17.5689$ (13) Å	$\mu = 0.40$ mm^{-1}
$\beta = 101.871$ (3)°	$T = 180$ K
$V = 956.89$ (12) Å^3	Block, brown
$Z = 2$	$0.35 \times 0.18 \times 0.13$ mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer	2789 independent reflections
	2537 reflections with $I > 2\sigma(I)$
Detector resolution: 10.000 pixels mm^{-1}	$R_{int} = 0.021$
ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 3.3°$
Absorption correction: numerical (*NUMABS*; Higashi, 1999)	$h = -21 \rightarrow 21$
	$k = -5 \rightarrow 4$
$T_{min} = 0.896$, $T_{max} = 0.949$	$l = -24 \rightarrow 24$
17752 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.030$	
$wR(F^2) = 0.079$	Secondary atom site location: difference Fourier map
$S = 1.11$	
2789 reflections	Hydrogen site location: difference Fourier map
176 parameters	H atoms treated by a mixture of independent and constrained refinement
8 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.3065P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.54$ e Å⁻³
$\Delta\rho_{min} = -0.24$ 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)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Cl1	0.48813 (2)	0.21752 (7)	0.32764 (2)	0.01728 (8)	
O1	0.64061 (5)	0.6016 (2)	0.43110 (4)	0.02004 (16)	
O2	0.34886 (5)	0.1370 (2)	0.42588 (4)	0.02038 (17)	
H2	0.317 (2)	0.137 (9)	0.4593 (16)	0.031*	0.5
O3	0.06134 (7)	0.3759 (3)	0.54909 (5)	0.0313 (2)	
H3	0.018 (2)	0.445 (12)	0.516 (2)	0.047*	0.5
O4	−0.03494 (6)	0.1653 (3)	0.62162 (5)	0.0303 (2)	
O5A	0.19794 (11)	0.1042 (7)	0.48308 (10)	0.0265 (4)	0.5
H9A	0.1547 (18)	0.038 (11)	0.4493 (18)	0.040*	0.5
H10A	0.2453 (15)	0.043 (11)	0.4682 (18)	0.040*	0.5
O5B	0.20132 (11)	−0.1191 (6)	0.48529 (9)	0.0199 (3)	0.5
H9B	0.1501 (15)	−0.090 (9)	0.4587 (19)	0.030*	0.5
H10B	0.209 (2)	−0.347 (5)	0.4873 (19)	0.030*	0.5
N1	0.19857 (6)	0.0209 (3)	0.63805 (5)	0.01977 (18)	
C1	0.57374 (6)	0.5511 (3)	0.45987 (5)	0.01438 (18)	
C2	0.49294 (7)	0.3688 (3)	0.42158 (5)	0.01476 (18)	
C3	0.42138 (6)	0.3090 (3)	0.45734 (6)	0.01574 (19)	
C4	0.12231 (7)	0.0793 (3)	0.66495 (6)	0.01658 (19)	
C5	0.12193 (7)	0.0166 (3)	0.74206 (6)	0.0198 (2)	
H5	0.068573	0.056090	0.761605	0.024*	
C6	0.20078 (8)	−0.1057 (3)	0.79117 (6)	0.0226 (2)	
H6	0.201710	−0.146932	0.844701	0.027*	
C7	0.27772 (7)	−0.1668 (3)	0.76174 (7)	0.0226 (2)	
H7	0.331694	−0.251819	0.794609	0.027*	
C8	0.27478 (7)	−0.1023 (3)	0.68384 (7)	0.0236 (2)	
H8	0.326860	−0.145258	0.662656	0.028*	
C9	0.04024 (8)	0.2152 (3)	0.60747 (6)	0.0210 (2)	
H1	0.1993 (12)	0.049 (5)	0.5876 (10)	0.039 (4)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01956 (13)	0.02040 (13)	0.01184 (12)	−0.00159 (8)	0.00314 (8)	−0.00202 (8)
O1	0.0170 (3)	0.0273 (4)	0.0174 (3)	−0.0029 (3)	0.0071 (3)	−0.0028 (3)
O2	0.0159 (3)	0.0286 (4)	0.0168 (3)	−0.0068 (3)	0.0037 (3)	−0.0038 (3)
O3	0.0340 (5)	0.0363 (5)	0.0200 (4)	−0.0003 (4)	−0.0028 (3)	0.0107 (4)

O4	0.0212 (4)	0.0433 (5)	0.0243 (4)	0.0042 (4)	−0.0003 (3)	0.0001 (4)
O5A	0.0152 (8)	0.0467 (13)	0.0185 (8)	−0.0033 (8)	0.0052 (6)	−0.0080 (8)
O5B	0.0160 (7)	0.0243 (9)	0.0188 (7)	−0.0013 (7)	0.0028 (5)	−0.0010 (7)
N1	0.0231 (4)	0.0215 (4)	0.0160 (4)	0.0002 (4)	0.0071 (3)	−0.0002 (3)
C1	0.0148 (4)	0.0154 (4)	0.0132 (4)	0.0008 (3)	0.0035 (3)	0.0012 (3)
C2	0.0171 (4)	0.0174 (4)	0.0100 (4)	−0.0015 (3)	0.0033 (3)	−0.0007 (3)
C3	0.0147 (4)	0.0186 (5)	0.0137 (4)	0.0012 (4)	0.0025 (3)	0.0021 (3)
C4	0.0177 (4)	0.0163 (4)	0.0151 (4)	−0.0002 (4)	0.0022 (3)	0.0005 (3)
C5	0.0183 (4)	0.0251 (5)	0.0166 (4)	0.0003 (4)	0.0052 (3)	0.0026 (4)
C6	0.0236 (5)	0.0271 (6)	0.0163 (4)	−0.0015 (4)	0.0018 (4)	0.0051 (4)
C7	0.0185 (5)	0.0209 (5)	0.0261 (5)	0.0010 (4)	−0.0009 (4)	0.0032 (4)
C8	0.0197 (5)	0.0245 (5)	0.0281 (5)	0.0025 (4)	0.0083 (4)	−0.0013 (4)
C9	0.0241 (5)	0.0207 (5)	0.0156 (4)	0.0022 (4)	−0.0017 (4)	−0.0013 (4)

Geometric parameters (Å, º)

Cl1—C2	1.7293 (9)	N1—H1	0.895 (18)
O1—C1	1.2330 (11)	C1—C2	1.4335 (13)
O2—C3	1.2875 (12)	C1—C3[i]	1.5307 (13)
O2—H2	0.830 (18)	C2—C3	1.3751 (13)
O3—C9	1.2801 (14)	C4—C5	1.3754 (13)
O3—H3	0.814 (17)	C4—C9	1.5139 (14)
O4—C9	1.2250 (15)	C5—C6	1.3939 (15)
O5A—H9A	0.824 (18)	C5—H5	0.9500
O5A—H10A	0.841 (18)	C6—C7	1.3840 (16)
O5B—H9B	0.824 (17)	C6—H6	0.9500
O5B—H10B	0.849 (17)	C7—C8	1.3808 (16)
N1—C8	1.3406 (14)	C7—H7	0.9500
N1—C4	1.3492 (13)	C8—H8	0.9500
C3—O2—H2	105 (2)	N1—C4—C9	117.38 (9)
C9—O3—H3	115 (3)	C5—C4—C9	122.95 (9)
H9A—O5A—H10A	107 (3)	C4—C5—C6	119.20 (9)
H9B—O5B—H10B	105 (3)	C4—C5—H5	120.4
C8—N1—C4	122.23 (9)	C6—C5—H5	120.4
C8—N1—H1	116.7 (11)	C7—C6—C5	119.83 (10)
C4—N1—H1	120.9 (11)	C7—C6—H6	120.1
O1—C1—C2	124.63 (9)	C5—C6—H6	120.1
O1—C1—C3[i]	117.08 (9)	C8—C7—C6	118.95 (10)
C2—C1—C3[i]	118.29 (8)	C8—C7—H7	120.5
C3—C2—C1	122.26 (8)	C6—C7—H7	120.5
C3—C2—Cl1	120.12 (8)	N1—C8—C7	120.11 (10)
C1—C2—Cl1	117.62 (7)	N1—C8—H8	119.9
O2—C3—C2	124.19 (9)	C7—C8—H8	119.9
O2—C3—C1[i]	116.38 (8)	O4—C9—O3	128.74 (11)
C2—C3—C1[i]	119.43 (8)	O4—C9—C4	118.74 (10)
N1—C4—C5	119.67 (9)	O3—C9—C4	112.51 (10)

O1—C1—C2—C3	177.79 (10)	N1—C4—C5—C6	0.18 (17)
C3^i—C1—C2—C3	−1.60 (16)	C9—C4—C5—C6	−179.46 (10)
O1—C1—C2—Cl1	−1.39 (14)	C4—C5—C6—C7	−0.86 (17)
C3^i—C1—C2—Cl1	179.22 (7)	C5—C6—C7—C8	0.46 (18)
C1—C2—C3—O2	−177.81 (10)	C4—N1—C8—C7	−1.34 (17)
Cl1—C2—C3—O2	1.35 (15)	C6—C7—C8—N1	0.62 (18)
C1—C2—C3—C1^i	1.61 (16)	N1—C4—C9—O4	157.55 (11)
Cl1—C2—C3—C1^i	−179.22 (7)	C5—C4—C9—O4	−22.81 (16)
C8—N1—C4—C5	0.93 (17)	N1—C4—C9—O3	−23.17 (14)
C8—N1—C4—C9	−179.41 (10)	C5—C4—C9—O3	156.48 (11)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5A	0.895 (17)	1.843 (17)	2.7380 (19)	179 (2)
N1—H1···O5B	0.895 (17)	1.907 (17)	2.7417 (18)	154.4 (17)
O2—H2···O5B	0.83 (3)	2.12 (3)	2.8111 (19)	141 (3)
O3—H3···O3^{ii}	0.82 (3)	1.62 (4)	2.4352 (14)	174 (4)
O5A—H9A···O4^{iii}	0.82 (3)	2.11 (3)	2.927 (2)	170 (3)
O5B—H9B···O4^{iii}	0.82 (3)	2.02 (3)	2.8159 (19)	162 (3)
O5A—H10A···O2	0.84 (3)	1.90 (3)	2.6762 (19)	154 (4)
O5B—H10B···O1^{iv}	0.85 (2)	2.60 (3)	3.095 (2)	119 (2)
C8—H8···Cl1^{iv}	0.95	2.78	3.6524 (12)	154
C8—H8···O1^{iv}	0.95	2.47	3.1871 (14)	132

Symmetry codes: (ii) −x, −y+1, −z+1; (iii) −x, −y, −z+1; (iv) −x+1, −y, −z+1.

chloranilic acid–2-carboxyquinoline (1/2) dihydrate (II)

Crystal data

2C$_{10}$H$_7$NO$_2$·C$_6$H$_2$Cl$_2$O$_4$·2H$_2$O
$M_r = 591.36$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 4.4745$ (2) Å
$b = 10.5448$ (8) Å
$c = 13.6111$ (6) Å
$\alpha = 96.652$ (4)°
$\beta = 94.109$ (3)°
$\gamma = 99.009$ (4)°
$V = 627.38$ (6) Å^3

$Z = 1$
$F(000) = 304.00$
$D_x = 1.565$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 9714 reflections
$\theta = 3.0$–30.1°
$\mu = 0.32$ mm^{-1}
$T = 200$ K
Platelet, brown
$0.41 \times 0.21 \times 0.03$ mm

Data collection

Rigaku R-AXIS RAPIDII
   diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: numerical
   (*NUMABS*; Higashi, 1999)
$T_{min} = 0.925$, $T_{max} = 0.990$
12358 measured reflections

3666 independent reflections
2755 reflections with $I > 2\sigma(I)$
$R_{int} = 0.122$
$\theta_{max} = 30.0°$, $\theta_{min} = 3.0°$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier
$R[F^2 > 2\sigma(F^2)] = 0.052$	map
$wR(F^2) = 0.149$	Hydrogen site location: inferred from
$S = 1.00$	neighbouring sites
3666 reflections	H atoms treated by a mixture of independent
197 parameters	and constrained refinement
2 restraints	$w = 1/[\sigma^2(F_o^2) + (0.0879P)^2]$
Primary atom site location: structure-invariant	where $P = (F_o^2 + 2F_c^2)/3$
direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.52$ e Å^{-3}
	$\Delta\rho_{min} = -0.45$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cl1	0.49390 (9)	0.23664 (4)	−0.02842 (3)	0.04300 (16)
O1	0.0319 (3)	0.08081 (12)	−0.17653 (8)	0.0426 (3)
O2	0.4150 (3)	0.11710 (11)	0.15510 (9)	0.0391 (3)
O3	−0.1769 (3)	0.36216 (11)	0.47121 (9)	0.0372 (3)
O4	−0.0712 (3)	0.16160 (11)	0.43604 (9)	0.0425 (3)
O5	0.3938 (3)	0.07471 (12)	0.33231 (9)	0.0406 (3)
N1	0.3233 (3)	0.41970 (12)	0.60390 (9)	0.0298 (3)
C1	0.0207 (3)	0.04635 (14)	−0.09469 (11)	0.0317 (3)
C2	0.2276 (3)	0.10762 (14)	−0.00985 (11)	0.0320 (3)
C3	0.2197 (3)	0.06514 (14)	0.07971 (11)	0.0313 (3)
C4	0.2151 (3)	0.29703 (14)	0.56909 (11)	0.0305 (3)
C5	0.3274 (3)	0.19702 (15)	0.61140 (11)	0.0336 (3)
H5	0.250293	0.109195	0.586437	0.040*
C6	0.5493 (4)	0.22680 (15)	0.68906 (12)	0.0342 (3)
H6	0.622423	0.159293	0.719133	0.041*
C7	0.6694 (3)	0.35659 (14)	0.72449 (11)	0.0312 (3)
C8	0.9050 (4)	0.39332 (16)	0.80217 (12)	0.0363 (3)
H8	0.985438	0.328869	0.834065	0.044*
C9	1.0170 (4)	0.52094 (18)	0.83147 (13)	0.0411 (4)
H9	1.175836	0.545100	0.883608	0.049*
C10	0.8980 (4)	0.61764 (17)	0.78463 (13)	0.0418 (4)
H10	0.980263	0.706066	0.805678	0.050*
C11	0.6677 (4)	0.58722 (15)	0.70983 (13)	0.0372 (3)
H11	0.587483	0.653070	0.679646	0.045*
C12	0.5532 (3)	0.45558 (14)	0.67897 (10)	0.0294 (3)
C13	−0.0333 (3)	0.27243 (14)	0.48397 (11)	0.0315 (3)
H1	0.252 (5)	0.481 (2)	0.5760 (17)	0.055 (6)*
H2	0.359 (7)	0.083 (3)	0.216 (2)	0.092 (10)*

H3	0.255 (4)	0.086 (2)	0.3667 (15)	0.054 (6)*
H4	0.560 (4)	0.111 (2)	0.3651 (17)	0.063 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0402 (2)	0.0380 (2)	0.0465 (2)	−0.00570 (16)	−0.00095 (18)	0.00725 (17)
O1	0.0451 (7)	0.0452 (7)	0.0354 (6)	0.0008 (5)	−0.0026 (5)	0.0093 (5)
O2	0.0388 (6)	0.0380 (6)	0.0359 (6)	−0.0005 (5)	−0.0079 (5)	0.0012 (4)
O3	0.0376 (6)	0.0319 (6)	0.0427 (6)	0.0068 (4)	−0.0017 (5)	0.0089 (4)
O4	0.0403 (6)	0.0368 (6)	0.0471 (6)	0.0091 (5)	−0.0071 (5)	−0.0052 (5)
O5	0.0400 (7)	0.0419 (7)	0.0357 (6)	0.0047 (5)	−0.0066 (5)	−0.0029 (5)
N1	0.0302 (6)	0.0269 (6)	0.0326 (6)	0.0053 (5)	0.0020 (5)	0.0055 (5)
C1	0.0292 (7)	0.0304 (7)	0.0353 (7)	0.0061 (5)	−0.0004 (6)	0.0039 (6)
C2	0.0287 (7)	0.0274 (7)	0.0384 (7)	0.0022 (5)	−0.0010 (6)	0.0032 (5)
C3	0.0298 (7)	0.0278 (7)	0.0354 (7)	0.0064 (5)	−0.0016 (6)	0.0007 (5)
C4	0.0297 (7)	0.0291 (7)	0.0330 (7)	0.0046 (5)	0.0044 (6)	0.0045 (5)
C5	0.0347 (7)	0.0273 (7)	0.0384 (7)	0.0043 (5)	0.0005 (6)	0.0051 (5)
C6	0.0357 (7)	0.0301 (7)	0.0378 (7)	0.0059 (6)	0.0020 (6)	0.0089 (6)
C7	0.0299 (7)	0.0315 (7)	0.0325 (7)	0.0047 (5)	0.0039 (6)	0.0054 (5)
C8	0.0347 (7)	0.0388 (8)	0.0353 (7)	0.0063 (6)	0.0011 (6)	0.0060 (6)
C9	0.0358 (8)	0.0453 (9)	0.0382 (8)	0.0033 (7)	−0.0036 (7)	−0.0030 (7)
C10	0.0402 (8)	0.0329 (8)	0.0484 (9)	0.0026 (6)	0.0006 (7)	−0.0046 (7)
C11	0.0376 (8)	0.0289 (7)	0.0443 (8)	0.0061 (6)	0.0027 (7)	0.0014 (6)
C12	0.0281 (6)	0.0287 (7)	0.0311 (6)	0.0044 (5)	0.0042 (6)	0.0021 (5)
C13	0.0293 (7)	0.0311 (7)	0.0339 (7)	0.0037 (5)	0.0024 (6)	0.0058 (5)

Geometric parameters (Å, º)

Cl1—C2	1.7174 (15)	C4—C13	1.517 (2)
O1—C1	1.2130 (18)	C5—C6	1.370 (2)
O2—C3	1.3070 (17)	C5—H5	0.9500
O2—H2	0.98 (3)	C6—C7	1.405 (2)
O3—C13	1.2453 (18)	C6—H6	0.9500
O4—C13	1.2512 (18)	C7—C8	1.413 (2)
O5—H3	0.821 (16)	C7—C12	1.420 (2)
O5—H4	0.848 (16)	C8—C9	1.363 (2)
N1—C4	1.3270 (19)	C8—H8	0.9500
N1—C12	1.3722 (19)	C9—C10	1.415 (3)
N1—H1	0.88 (2)	C9—H9	0.9500
C1—C2	1.447 (2)	C10—C11	1.368 (2)
C1—C3$^{\text{i}}$	1.507 (2)	C10—H10	0.9500
C2—C3	1.348 (2)	C11—C12	1.406 (2)
C4—C5	1.401 (2)	C11—H11	0.9500
C3—O2—H2	111.3 (18)	C7—C6—H6	119.8
H3—O5—H4	108 (2)	C6—C7—C8	123.01 (14)
C4—N1—C12	122.93 (13)	C6—C7—C12	118.61 (13)

C4—N1—H1	119.1 (16)	C8—C7—C12	118.37 (14)
C12—N1—H1	117.9 (16)	C9—C8—C7	120.18 (15)
O1—C1—C2	123.09 (14)	C9—C8—H8	119.9
O1—C1—C3ⁱ	118.94 (13)	C7—C8—H8	119.9
C2—C1—C3ⁱ	117.97 (13)	C8—C9—C10	120.32 (15)
C3—C2—C1	122.39 (13)	C8—C9—H9	119.8
C3—C2—Cl1	120.62 (11)	C10—C9—H9	119.8
C1—C2—Cl1	116.98 (11)	C11—C10—C9	121.78 (15)
O2—C3—C2	122.30 (14)	C11—C10—H10	119.1
O2—C3—C1ⁱ	118.13 (13)	C9—C10—H10	119.1
C2—C3—C1ⁱ	119.57 (12)	C10—C11—C12	118.00 (15)
N1—C4—C5	120.22 (13)	C10—C11—H11	121.0
N1—C4—C13	116.94 (13)	C12—C11—H11	121.0
C5—C4—C13	122.84 (13)	N1—C12—C11	120.39 (13)
C6—C5—C4	119.50 (14)	N1—C12—C7	118.27 (13)
C6—C5—H5	120.2	C11—C12—C7	121.34 (14)
C4—C5—H5	120.2	O3—C13—O4	128.04 (14)
C5—C6—C7	120.39 (14)	O3—C13—C4	117.19 (13)
C5—C6—H6	119.8	O4—C13—C4	114.76 (13)

O1—C1—C2—C3	−177.43 (15)	C12—C7—C8—C9	−0.4 (2)
C3ⁱ—C1—C2—C3	2.8 (2)	C7—C8—C9—C10	0.2 (3)
O1—C1—C2—Cl1	1.2 (2)	C8—C9—C10—C11	0.5 (3)
C3ⁱ—C1—C2—Cl1	−178.60 (10)	C9—C10—C11—C12	−1.0 (3)
C1—C2—C3—O2	177.00 (13)	C4—N1—C12—C11	177.18 (14)
Cl1—C2—C3—O2	−1.6 (2)	C4—N1—C12—C7	−3.2 (2)
C1—C2—C3—C1ⁱ	−2.8 (2)	C10—C11—C12—N1	−179.65 (14)
Cl1—C2—C3—C1ⁱ	178.61 (10)	C10—C11—C12—C7	0.7 (2)
C12—N1—C4—C5	2.4 (2)	C6—C7—C12—N1	1.5 (2)
C12—N1—C4—C13	−178.34 (12)	C8—C7—C12—N1	−179.66 (13)
N1—C4—C5—C6	0.1 (2)	C6—C7—C12—C11	−178.84 (14)
C13—C4—C5—C6	−179.12 (14)	C8—C7—C12—C11	0.0 (2)
C4—C5—C6—C7	−1.6 (2)	N1—C4—C13—O3	−19.8 (2)
C5—C6—C7—C8	−177.95 (14)	C5—C4—C13—O3	159.47 (14)
C5—C6—C7—C12	0.8 (2)	N1—C4—C13—O4	161.50 (14)
C6—C7—C8—C9	178.31 (16)	C5—C4—C13—O4	−19.3 (2)

Symmetry code: (i) −x, −y, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3ⁱⁱ	0.88 (2)	1.91 (2)	2.7724 (17)	167 (2)
O2—H2···O5	0.98 (3)	1.59 (3)	2.5092 (17)	155 (3)
O5—H3···O4	0.82 (2)	2.01 (2)	2.8072 (19)	164 (2)
O5—H4···O4ⁱⁱⁱ	0.85 (2)	1.82 (2)	2.6632 (19)	171 (2)

| C6—H6···O1[iv] | 0.95 | 2.54 | 3.392 (2) | 150 |
| C6—H6···O5[v] | 0.95 | 2.47 | 3.211 (2) | 134 |

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