Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Triethylammonium hydrogen chloranilate

Kazuma Gotoh, Shinpei Maruyama and Hiroyuki Ishida*

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan
Correspondence e-mail: ishidah@cc.okayama-u.ac.jp

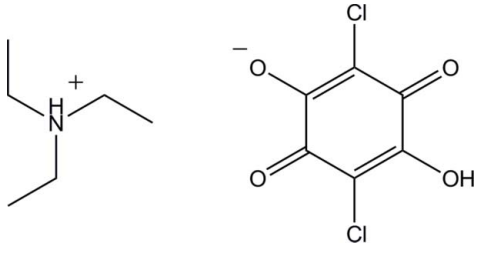
Received 1 November 2010; accepted 17 November 2010

Key indicators: single-crystal X-ray study; T = 180 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.092; data-to-parameter ratio = 23.2.

In the crystal structure of the title compound (systematic name: triethylammonium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate), $C_6H_{16}N^+\cdot C_6HCl_2O_4^-$, two hydrogen chloranilate anions are connected by a pair of bifurcated O—H···O hydrogen bonds into a dimeric unit. The triethylammonium cations are linked on both sides of the dimer *via* bifurcated N—H···O hydrogen bonds into a centrosymmetric 2:2 aggregate. The 2:2 aggregates are further linked by intermolecular C—H···O hydrogen bonds.

Related literature

For related structures, see, for example: Gotoh *et al.* (2008, 2009); Gotoh & Ishida (2009); Yang (2007). For details of the double π system of chloranilic acid, see: Andersen (1967); Benchekroun & Savariault (1995).



Experimental

Crystal data

$C_6H_{16}N^+\cdot C_6HCl_2O_4^-$
M_r = 310.18
Triclinic, $P\overline{1}$
a = 7.6404 (5) Å
b = 9.5352 (3) Å
c = 11.2976 (5) Å
α = 99.9621 (15)°
β = 108.732 (3)°
γ = 106.536 (3)°
V = 714.84 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 180 K
0.42 × 0.35 × 0.25 mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.829, T_{max} = 0.891
14757 measured reflections
4176 independent reflections
3631 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.092
S = 1.07
4176 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.847 (18)	2.411 (15)	2.9805 (12)	125.1 (13)
N1—H1···O4	0.847 (18)	2.069 (18)	2.8833 (12)	161.1 (14)
O2—H2···O3	0.765 (19)	2.147 (19)	2.6331 (11)	121.9 (17)
O2—H2···O3^{i}	0.765 (19)	2.082 (19)	2.7089 (12)	139.4 (19)
C7—H7*B*···O2^{ii}	0.99	2.47	3.2859 (15)	140
C8—H8*A*···O4^{iii}	0.98	2.47	3.3977 (14)	158

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

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 22550013) from the Japan Society for the Promotion of Science.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2739).

References

Andersen, E. K. (1967). *Acta Cryst.* **22**, 196–201.
Benchekroun, R. & Savariault, J.-M. (1995). *Acta Cryst.* C**51**, 186–188.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gotoh, K., Asaji, T. & Ishida, H. (2008). *Acta Cryst.* C**64**, o550–o553.
Gotoh, K. & Ishida, H. (2009). *Acta Cryst.* E**65**, o2467.
Gotoh, K., Nagoshi, H. & Ishida, H. (2009). *Acta Cryst.* C**65**, o273–o277.
Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC. (2004). *PROCESS-AUTO* and *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Yang, D.-J. (2007). *Acta Cryst.* E**63**, o2600.

supporting information

Acta Cryst. (2010). E**66**, o3255 [https://doi.org/10.1107/S1600536810047744]

Triethylammonium hydrogen chloranilate

Kazuma Gotoh, Shinpei Maruyama and Hiroyuki Ishida

S1. Comment

The title compound, (I), was prepared in order to extend our study on *D*—H···*A* hydrogen bonding (*D* = N, O, or C; *A* = N, O or Cl) in amine–chloranilic acid systems (Gotoh *et al.*, 2008,2009; Gotoh & Ishida, 2009). The crystal structure of bis(hexamethylenetetraminium) chloranilate tetrahydrate has been reported for the tertiary amine–chloranilic acid 2:1 system (Yang, 2007).

In the crystal structure of the title compound, an acid-base interaction involving proton transfer is observed between chloranilic acid and triethylamine, and two hydrogen chloranilate anions and two triethylammnoium cations are linked by bifurcated O—H···O and N—H···O hydrogen bonds (Table 1) to afford a centrosymmetric 2:2 aggregate (Fig. 1). The anion shows a characteristic structure of the double π system (Andersen, 1967; Benchekroun & Savariault, 1995) with two long C1—C6 [1.5442 (13) Å] and C3—C4 [1.5063 (13) Å] bonds. The O3—C4 and O4—C6 bonds [1.2529 (11) and 1.2510 (11) Å, respectively] in one π system are almost same and comparable to the O—C bonds in the dianion of bis-(hexamethylenetetraminium) chloranilate tetrahydrate (Yang, 2007). On the other hand, the O1—C1 and O2—C3 bonds [1.2199 (12) and 1.3324 (11) Å, respectively] in the other π system correspond to double and single bonds, respectively. The 2:2 aggregates are further linked by intermolecular C—H···O hydrogen bonds, forming a three-dimensional network (Fig. 2).

S2. Experimental

Single crystals were obtained by slow evaporation from an acetonitrile solution (25 ml) of chloranilic acid (97 mg) and triethylamine (42 mg) at room temperature.

S3. Refinement

C-bound H atoms were positioned geometrically (C—H = 0.98 or 0.99 Å) and refined as riding, allowing for free rotation of the methyl group. U_{iso}(H) values were set at 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The O– and N-bound H atoms were found in a difference Fourier map and refined isotropically. The refined O—H and N—H distances are 0.765 (19) and 0.847 (18) Å, respectively.

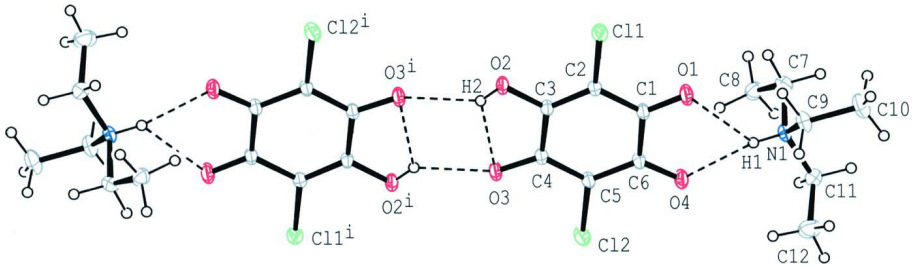


Figure 1

The molecular structure of the title compound, with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 35% probability level. The dashed lines indicate O—H···O and N—H···O hydrogen bonds. [Symmetry code: (i) -*x* + 1, -*y* + 2, -*z*].

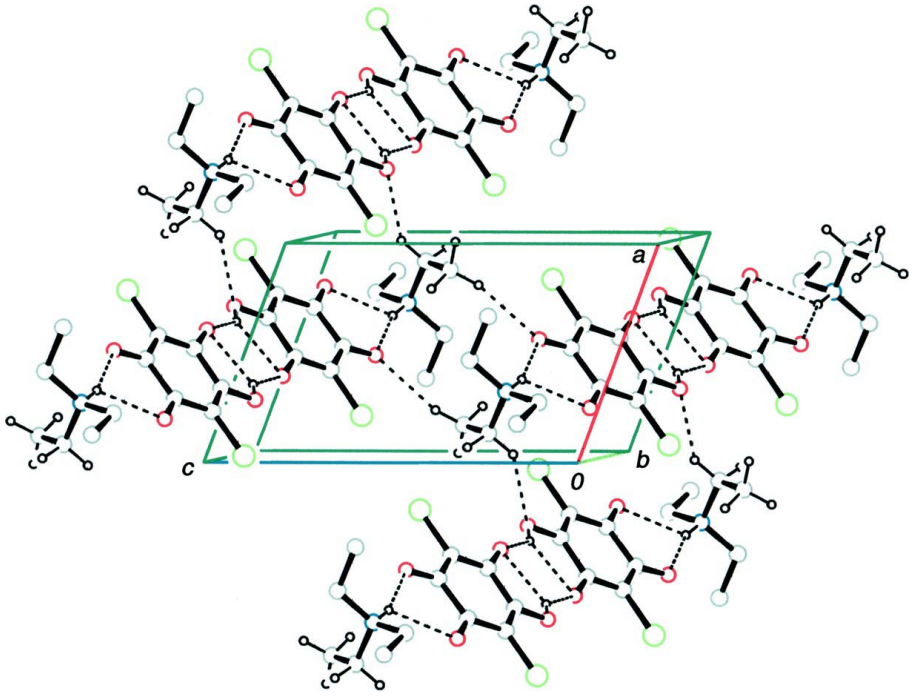


Figure 2

A partial packing diagram of the title compound. The dashed lines indicate O—H···O, N—H···O and C—H···O hydrogen bonds. H atoms of the ethyl groups not involved in the C—H···O hydrogen bonds have been omitted.

Triethylammonium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate

Crystal data

$C_6H_{16}N^+·C_6HCl_2O_4^-$
M_r = 310.18
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.6404 (5) Å
b = 9.5352 (3) Å
c = 11.2976 (5) Å
α = 99.9621 (15)°
β = 108.732 (3)°
γ = 106.536 (3)°
V = 714.84 (6) Å^3
Z = 2
F(000) = 324.00
D_x = 1.441 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 12766 reflections
θ = 3.0–30.1°
μ = 0.46 mm^{-1}

T = 180 K
Block, brown

0.42 × 0.35 × 0.25 mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.829, T_{max} = 0.891
14757 measured reflections

4176 independent reflections
3631 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 30.0°
h = −10→10
k = −13→13
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.092
S = 1.07
4176 reflections
180 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.1133P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.05941 (4)	0.44199 (3)	−0.17017 (2)	0.03282 (8)
Cl2	0.79265 (4)	0.85112 (3)	0.35611 (2)	0.03113 (8)
O1	0.23295 (13)	0.35023 (9)	0.06660 (8)	0.03546 (18)
O2	0.29888 (11)	0.77018 (9)	−0.10218 (8)	0.02849 (16)
O3	0.60830 (11)	0.93820 (8)	0.11497 (7)	0.02933 (16)
O4	0.53520 (12)	0.51893 (9)	0.29193 (8)	0.03090 (17)
N1	0.31226 (12)	0.21786 (9)	0.28996 (8)	0.02410 (16)
C1	0.31746 (14)	0.48352 (11)	0.07566 (9)	0.02382 (18)
C2	0.25857 (14)	0.55307 (11)	−0.02828 (9)	0.02340 (18)
C3	0.35511 (14)	0.70234 (11)	−0.01071 (9)	0.02249 (18)
C4	0.53096 (14)	0.80246 (10)	0.11283 (9)	0.02232 (17)
C5	0.59095 (14)	0.73644 (11)	0.21385 (9)	0.02326 (18)
C6	0.49384 (14)	0.58366 (11)	0.20508 (9)	0.02325 (18)
C7	0.12245 (15)	0.22545 (12)	0.29816 (11)	0.0307 (2)

H7A	0.0632	0.1399	0.3289	0.037*
H7B	0.0275	0.2125	0.2098	0.037*
C8	0.15318 (17)	0.37395 (13)	0.38885 (11)	0.0323 (2)
H8A	0.2209	0.3765	0.4795	0.048*
H8B	0.0242	0.3827	0.3768	0.048*
H8C	0.2344	0.4594	0.3693	0.048*
C9	0.27183 (18)	0.08580 (12)	0.17789 (11)	0.0320 (2)
H9A	0.3979	0.0937	0.1676	0.038*
H9B	0.1802	0.0938	0.0967	0.038*
C10	0.1828 (2)	−0.06935 (13)	0.19402 (15)	0.0435 (3)
H10A	0.2787	−0.0831	0.2686	0.065*
H10B	0.1502	−0.1493	0.1145	0.065*
H10C	0.0619	−0.0762	0.2094	0.065*
C11	0.45590 (16)	0.22080 (13)	0.41806 (11)	0.0313 (2)
H11A	0.3995	0.1271	0.4406	0.038*
H11B	0.4747	0.3098	0.4872	0.038*
C12	0.65531 (19)	0.23066 (17)	0.41462 (15)	0.0461 (3)
H12A	0.6413	0.1348	0.3574	0.069*
H12B	0.7501	0.2480	0.5031	0.069*
H12C	0.7037	0.3156	0.3811	0.069*
H1	0.365 (2)	0.2974 (19)	0.2713 (14)	0.037 (4)*
H2	0.364 (3)	0.855 (2)	−0.0717 (17)	0.055 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.03108 (13)	0.02407 (13)	0.03098 (14)	0.00336 (10)	0.00192 (10)	0.00952 (9)
Cl2	0.03405 (14)	0.02543 (13)	0.02406 (13)	0.00126 (10)	0.00727 (10)	0.00770 (9)
O1	0.0406 (4)	0.0198 (4)	0.0355 (4)	0.0021 (3)	0.0070 (3)	0.0134 (3)
O2	0.0304 (4)	0.0204 (4)	0.0303 (4)	0.0052 (3)	0.0067 (3)	0.0140 (3)
O3	0.0342 (4)	0.0184 (3)	0.0333 (4)	0.0056 (3)	0.0114 (3)	0.0128 (3)
O4	0.0353 (4)	0.0252 (4)	0.0283 (4)	0.0050 (3)	0.0091 (3)	0.0153 (3)
N1	0.0257 (4)	0.0190 (4)	0.0277 (4)	0.0046 (3)	0.0123 (3)	0.0098 (3)
C1	0.0266 (4)	0.0192 (4)	0.0267 (4)	0.0069 (3)	0.0112 (3)	0.0101 (3)
C2	0.0235 (4)	0.0195 (4)	0.0255 (4)	0.0059 (3)	0.0079 (3)	0.0088 (3)
C3	0.0244 (4)	0.0203 (4)	0.0257 (4)	0.0082 (3)	0.0113 (3)	0.0109 (3)
C4	0.0252 (4)	0.0183 (4)	0.0262 (4)	0.0076 (3)	0.0124 (3)	0.0092 (3)
C5	0.0260 (4)	0.0193 (4)	0.0230 (4)	0.0051 (3)	0.0094 (3)	0.0083 (3)
C6	0.0261 (4)	0.0206 (4)	0.0249 (4)	0.0069 (3)	0.0117 (3)	0.0103 (3)
C7	0.0232 (4)	0.0292 (5)	0.0376 (5)	0.0063 (4)	0.0120 (4)	0.0104 (4)
C8	0.0319 (5)	0.0344 (6)	0.0357 (5)	0.0164 (4)	0.0144 (4)	0.0131 (4)
C9	0.0415 (6)	0.0214 (5)	0.0327 (5)	0.0066 (4)	0.0187 (4)	0.0070 (4)
C10	0.0536 (7)	0.0218 (5)	0.0571 (8)	0.0075 (5)	0.0306 (6)	0.0101 (5)
C11	0.0301 (5)	0.0330 (5)	0.0312 (5)	0.0120 (4)	0.0103 (4)	0.0127 (4)
C12	0.0337 (6)	0.0490 (8)	0.0561 (8)	0.0214 (5)	0.0146 (5)	0.0117 (6)

Geometric parameters (Å, º)

Cl1—C2	1.7133 (10)	C7—H7A	0.9900
Cl2—C5	1.7307 (10)	C7—H7B	0.9900
O1—C1	1.2199 (12)	C8—H8A	0.9800
O2—C3	1.3324 (11)	C8—H8B	0.9800
O2—H2	0.766 (18)	C8—H8C	0.9800
O3—C4	1.2529 (11)	C9—C10	1.5115 (16)
O4—C6	1.2510 (11)	C9—H9A	0.9900
N1—C11	1.4993 (13)	C9—H9B	0.9900
N1—C9	1.5033 (13)	C10—H10A	0.9800
N1—C7	1.5036 (13)	C10—H10B	0.9800
N1—H1	0.847 (16)	C10—H10C	0.9800
C1—C2	1.4564 (13)	C11—C12	1.5130 (16)
C1—C6	1.5442 (13)	C11—H11A	0.9900
C2—C3	1.3490 (13)	C11—H11B	0.9900
C3—C4	1.5063 (13)	C12—H12A	0.9800
C4—C5	1.4092 (13)	C12—H12B	0.9800
C5—C6	1.4036 (13)	C12—H12C	0.9800
C7—C8	1.5047 (16)		

C3—O2—H2	106.0 (13)	C7—C8—H8A	109.5
C11—N1—C9	113.52 (8)	C7—C8—H8B	109.5
C11—N1—C7	111.98 (8)	H8A—C8—H8B	109.5
C9—N1—C7	111.23 (8)	C7—C8—H8C	109.5
C11—N1—H1	107.6 (10)	H8A—C8—H8C	109.5
C9—N1—H1	105.4 (10)	H8B—C8—H8C	109.5
C7—N1—H1	106.5 (10)	N1—C9—C10	114.04 (9)
O1—C1—C2	123.39 (9)	N1—C9—H9A	108.7
O1—C1—C6	118.01 (8)	C10—C9—H9A	108.7
C2—C1—C6	118.60 (8)	N1—C9—H9B	108.7
C3—C2—C1	120.43 (9)	C10—C9—H9B	108.7
C3—C2—Cl1	121.32 (7)	H9A—C9—H9B	107.6
C1—C2—Cl1	118.21 (7)	C9—C10—H10A	109.5
O2—C3—C2	121.58 (9)	C9—C10—H10B	109.5
O2—C3—C4	115.99 (8)	H10A—C10—H10B	109.5
C2—C3—C4	122.42 (8)	C9—C10—H10C	109.5
O3—C4—C5	126.59 (9)	H10A—C10—H10C	109.5
O3—C4—C3	115.62 (8)	H10B—C10—H10C	109.5
C5—C4—C3	117.79 (8)	N1—C11—C12	112.26 (10)
C6—C5—C4	123.24 (9)	N1—C11—H11A	109.2
C6—C5—Cl2	118.80 (7)	C12—C11—H11A	109.2
C4—C5—Cl2	117.95 (7)	N1—C11—H11B	109.2
O4—C6—C5	126.67 (9)	C12—C11—H11B	109.2
O4—C6—C1	115.87 (8)	H11A—C11—H11B	107.9
C5—C6—C1	117.46 (8)	C11—C12—H12A	109.5
N1—C7—C8	112.65 (8)	C11—C12—H12B	109.5
N1—C7—H7A	109.1	H12A—C12—H12B	109.5

C8—C7—H7A	109.1	C11—C12—H12C	109.5
N1—C7—H7B	109.1	H12A—C12—H12C	109.5
C8—C7—H7B	109.1	H12B—C12—H12C	109.5
H7A—C7—H7B	107.8		

O1—C1—C2—C3	178.24 (10)	C3—C4—C5—Cl2	−179.88 (7)
C6—C1—C2—C3	−0.79 (14)	C4—C5—C6—O4	−177.80 (10)
O1—C1—C2—Cl1	0.38 (14)	Cl2—C5—C6—O4	1.38 (15)
C6—C1—C2—Cl1	−178.65 (7)	C4—C5—C6—C1	2.18 (14)
C1—C2—C3—O2	−177.16 (9)	Cl2—C5—C6—C1	−178.64 (6)
Cl1—C2—C3—O2	0.63 (14)	O1—C1—C6—O4	−0.58 (14)
C1—C2—C3—C4	2.41 (15)	C2—C1—C6—O4	178.50 (9)
Cl1—C2—C3—C4	−179.80 (7)	O1—C1—C6—C5	179.44 (9)
O2—C3—C4—O3	−1.57 (12)	C2—C1—C6—C5	−1.48 (13)
C2—C3—C4—O3	178.84 (9)	C11—N1—C7—C8	64.50 (11)
O2—C3—C4—C5	177.84 (8)	C9—N1—C7—C8	−167.30 (9)
C2—C3—C4—C5	−1.75 (14)	C11—N1—C9—C10	60.54 (13)
O3—C4—C5—C6	178.64 (9)	C7—N1—C9—C10	−66.83 (13)
C3—C4—C5—C6	−0.70 (14)	C9—N1—C11—C12	59.27 (12)
O3—C4—C5—Cl2	−0.55 (14)	C7—N1—C11—C12	−173.75 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.847 (18)	2.411 (15)	2.9805 (12)	125.1 (13)
N1—H1···O4	0.847 (18)	2.069 (18)	2.8833 (12)	161.1 (14)
O2—H2···O3	0.765 (19)	2.147 (19)	2.6331 (11)	121.9 (17)
O2—H2···O3^{i}	0.765 (19)	2.082 (19)	2.7089 (12)	139.4 (19)
C7—H7*B*···O2^{ii}	0.99	2.47	3.2859 (15)	140
C8—H8*A*···O4^{iii}	0.98	2.47	3.3977 (14)	158

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) −*x*, −*y*+1, −*z*; (iii) −*x*+1, −*y*+1, −*z*+1.