Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Chloroanilinium perchlorate–18-crown-16 (1/1)

Chun-Hua Yu

Ordered Matter Science Research Center, Collenge of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People's Republic of China
Correspondence e-mail: jxyuchunhua@163.com

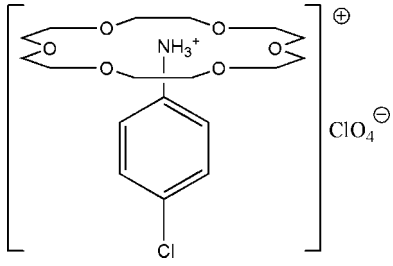
Received 24 October 2011; accepted 16 November 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.114; data-to-parameter ratio = 18.2.

In the title compound, $C_6H_7ClN^+\cdot ClO_4^-\cdot C_{12}H_{24}O_6$, the cation forms a 1:1 complex with the crown ether, *viz* $[C_6H_7ClN$-(18-crown-6)$]^+$, in which the $-NH_3^+$ unit nests in the crown and interacts with it through bifurcated N—H···O hydrogen bonding. All constituents of the structure have crystallographically imposed mirror symmetry except for the H atoms of the $-NH_3^+$ group which are disordered across the mirror.

Related literature

The title compound was synthesized as part of a study aimed at finding new ferroelectric materials. For general background to ferroelectric compounds, see: Fu *et al.* (2009); Ye *et al.* (2006); Zhang, Xiong *et al.* (2008); Zhang, Ye *et al.* (2010). For background to crown ether/ammonium ion complexes, see: Fender *et al.* (2002); Kryatova *et al.* (2004).



Experimental

Crystal data

$C_6H_7ClN^+\cdot ClO_4^-\cdot C_{12}H_{24}O_6$
M_r = 492.34
Orthorhombic, *Pnma*
a = 15.726 (3) Å
b = 11.525 (2) Å
c = 12.896 (3) Å
V = 2337.3 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 293 K
0.35 × 0.32 × 0.28 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.891, T_{max} = 0.912
23203 measured reflections
2820 independent reflections
2231 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.114
S = 1.08
2820 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 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—H1A···O4	0.89	2.14	2.896 (3)	142
N1—H1A···O3^{i}	0.89	2.21	2.9311 (17)	138
N1—H1B···O2^{i}	0.89	2.14	2.8952 (18)	143
N1—H1B···O1	0.89	2.18	2.870 (3)	134
N1—H1C···O2	0.89	2.15	2.8952 (18)	140
N1—H1C···O3	0.89	2.20	2.9311 (17)	139

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The author thanks the Ordered Matter Science Research Centre, Southeast University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MW2036).

References

Fender, N. S., Kahwa, I. A. & Fronczek, F. R. (2002). *J. Solid State Chem.* **163**, 286–293.
Fu, D.-W., Ge, J.-Z., Dai, J., Ye, H.-Y. & Qu, Z.-R. (2009). *Inorg. Chem. Commun.* **12**, 994–997.
Kryatova, O. P., Korendovych, I. V. & Rybak-Akimova, E. V. (2004). *Tetrahedron*, **60**, 4579–4588.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ye, Q., Song, Y.-M., Wang, G.-X., Chen, K., Fu, D.-W., Chan, P. W. H., Zhu, J.-S., Huang, S.-P. D. & Xiong, R.-G. (2006). *J. Am. Chem. Soc.* **128**, 6554–6555.
Zhang, W., Xiong, R.-G. & Huang, S.-P. D. (2008). *J. Am. Chem. Soc.* **130**, 10468–10469.
Zhang, W., Ye, H.-Y., Cai, H.-L., Ge, J.-Z., Xiong, R.-G. & Huang, S.-P. D. (2010). *J. Am. Chem. Soc.* **132**, 7300–7302.

supporting information

Acta Cryst. (2011). E**67**, o3400 [https://doi.org/10.1107/S1600536811048859]

4-Chloroanilinium perchlorate–18-crown-16 (1/1)

Chun-Hua Yu

S1. Comment

We synthesized the title compound, (I), with the aim of finding new ferroelectric materials (Fu *et al.*, 2009; Ye *et al.*, 2006; Zhang, Xiong *et al.*, 2008; Zhang, Ye *et al.*, 2010). There is currently a significant interest in crown ethers because of their ability to form noncovalent, hydrogen bonding complexes with ammonium cations both in the solid state and in solution (Fender *et al.*, 2002; Kryatova *et al.*, 2004). In the crystal, the *p*-chloroanilium cations and 18-crown-6 molecules are associated *via* hydrogen bonding with the $–NH_3^+$ group forming bifurcated hydrogen bonds with all six O atoms of the crown ether molecule (Figure 1, Table 1). Despite the disorder in the $–NH_3^+$ group, it is clear that in each orientation the cation forms three bifurcated hydrogen bonds.

S2. Experimental

p-chloroaniline (1.28 g, 10 mmol) was dissolved in *N*,*N*-dimethyl formamide(DMF) (10 ml) to which an aqueous solution of perchloric acid was dropped slowly with stirring until the pH of the solution was *ca* 7. 18-crown-6 (2.64 g 10 mmol) was added to the solution and more DMF was added until the initial precipitate dissolved. The solution was filtered to a clean beaker and massive crystals of (I) were obtained *via* slow evaporation of the DMF solution at room temperature over several weeks.

S3. Refinement

H atoms attached to C were placed in calculated positions (C—H = 0.93 Å for Csp^2 atoms and 0.97 Å for Csp^3 atoms) while those attached to N were placed in positions derived from a difference map and the N—H distances adjusted to 0.89 Å. All were included as riding contributions with U_{iso} values tied to those of the attached atoms (U_{iso} = 1.2Ueq(Csp^2/N) and 1.5Ueq(Csp^3)).

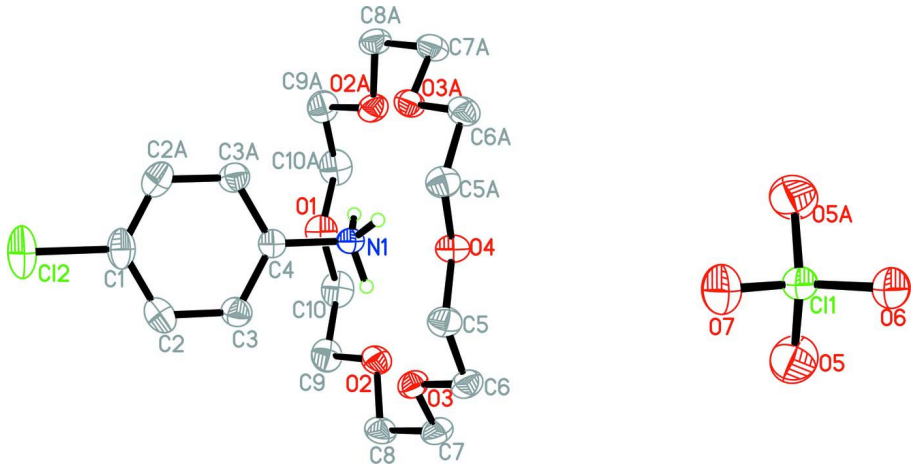


Figure 1

Perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

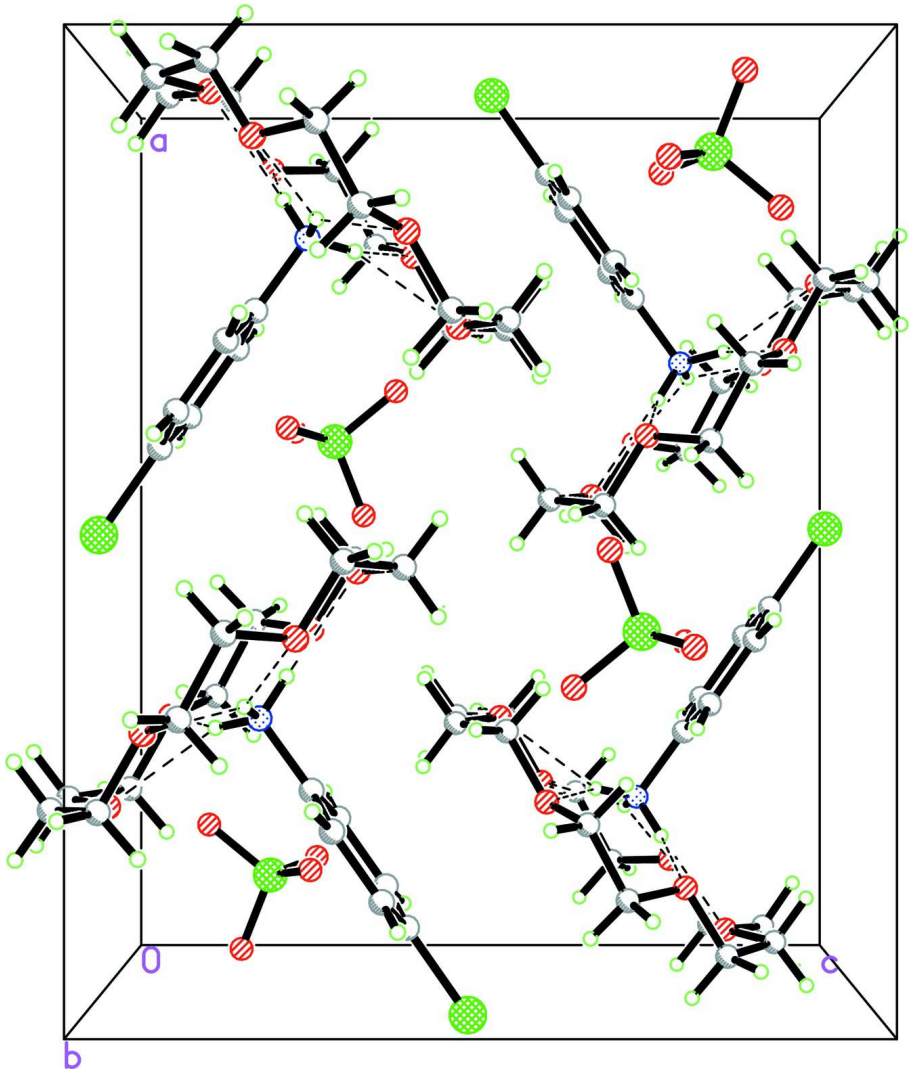


Figure 2

A view of the packing of the title compound down the *b* axis. Dashed lines indicate hydrogen bonds.

4-Chloroanilinium perchlorate–18-crown-16 (1/1)

Crystal data

$C_6H_7ClN^+\cdot ClO_4^-\cdot C_{12}H_{24}O_6$
$M_r = 492.34$
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
$a = 15.726\ (3)$ Å
$b = 11.525\ (2)$ Å
$c = 12.896\ (3)$ Å
$V = 2337.3\ (8)$ Å^3
$Z = 4$
$F(000) = 1040$
$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2820 reflections
$\theta = 3.0–27.5°$
$\mu = 0.33$ mm^{-1}
$T = 293$ K
Block, colorless
0.35 × 0.32 × 0.28 mm

Data collection

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.891, T_{max} = 0.912
23203 measured reflections
2820 independent reflections
2231 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −20→20
k = −14→14
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.114
S = 1.08
2820 reflections
155 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.9195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0159 (11)

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}	Occ. (<1)
C1	0.91237 (18)	0.2500	0.5933 (2)	0.0575 (8)	
C2	0.87729 (13)	0.1459 (2)	0.62262 (16)	0.0587 (5)	
H2	0.9016	0.0763	0.6014	0.070*	
C3	0.80513 (12)	0.14605 (17)	0.68421 (15)	0.0500 (5)	
H3	0.7808	0.0764	0.7052	0.060*	
C4	0.76968 (15)	0.2500	0.71422 (17)	0.0378 (5)	
C5	0.53619 (13)	0.14754 (16)	0.59540 (14)	0.0496 (5)	
H5A	0.5865	0.1403	0.5524	0.059*	
H5B	0.4868	0.1508	0.5504	0.059*	
C6	0.52948 (12)	0.04615 (17)	0.66648 (16)	0.0512 (5)	
H6A	0.4820	0.0570	0.7135	0.061*	
H6B	0.5194	−0.0239	0.6266	0.061*	
C7	0.59921 (13)	−0.04958 (17)	0.80440 (16)	0.0544 (5)	
H7A	0.5829	−0.1238	0.7751	0.065*	
H7B	0.5557	−0.0262	0.8535	0.065*	

C8	0.68241 (13)	−0.06071 (17)	0.85833 (16)	0.0545 (5)	
H8A	0.6801	−0.1240	0.9079	0.065*	
H8B	0.7269	−0.0775	0.8084	0.065*	
C9	0.77936 (13)	0.0436 (2)	0.96481 (17)	0.0600 (6)	
H9A	0.8262	0.0451	0.9158	0.072*	
H9B	0.7837	−0.0269	1.0056	0.072*	
C10	0.78372 (15)	0.1468 (2)	1.03395 (16)	0.0644 (6)	
H10A	0.7344	0.1485	1.0791	0.077*	
H10B	0.8342	0.1423	1.0770	0.077*	
Cl1	0.10405 (4)	0.2500	0.20475 (5)	0.0469 (2)	
Cl2	1.00340 (6)	0.2500	0.51600 (8)	0.0976 (4)	
N1	0.69437 (12)	0.2500	0.78054 (15)	0.0387 (5)	
H1A	0.6518	0.2853	0.7478	0.046*	0.50
H1B	0.7058	0.2875	0.8392	0.046*	0.50
H1C	0.6796	0.1772	0.7949	0.046*	0.50
O1	0.78626 (12)	0.2500	0.97279 (13)	0.0544 (5)	
O2	0.70060 (8)	0.04546 (12)	0.91065 (11)	0.0527 (4)	
O3	0.60630 (8)	0.03499 (11)	0.72394 (10)	0.0478 (3)	
O4	0.54115 (12)	0.2500	0.65597 (13)	0.0455 (4)	
O5	0.11758 (11)	0.14801 (15)	0.26549 (15)	0.0858 (6)	
O6	0.01894 (12)	0.2500	0.16435 (17)	0.0607 (6)	
O7	0.16221 (14)	0.2500	0.11884 (19)	0.0741 (6)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0407 (14)	0.090 (2)	0.0422 (15)	0.000	−0.0008 (12)	0.000
C2	0.0585 (12)	0.0672 (14)	0.0505 (11)	0.0166 (10)	0.0025 (10)	−0.0023 (10)
C3	0.0553 (11)	0.0468 (11)	0.0479 (10)	0.0032 (9)	0.0018 (9)	0.0011 (8)
C4	0.0391 (12)	0.0444 (13)	0.0300 (11)	0.000	−0.0071 (10)	0.000
C5	0.0565 (11)	0.0473 (11)	0.0449 (10)	−0.0017 (9)	−0.0074 (9)	−0.0085 (8)
C6	0.0509 (11)	0.0433 (11)	0.0593 (12)	−0.0099 (8)	−0.0062 (9)	−0.0063 (9)
C7	0.0625 (12)	0.0391 (10)	0.0615 (12)	−0.0065 (9)	0.0045 (10)	0.0074 (9)
C8	0.0642 (12)	0.0384 (10)	0.0608 (12)	0.0091 (9)	0.0062 (10)	0.0101 (9)
C9	0.0535 (12)	0.0660 (14)	0.0605 (13)	0.0097 (10)	−0.0093 (10)	0.0190 (11)
C10	0.0638 (13)	0.0852 (17)	0.0443 (11)	0.0034 (12)	−0.0125 (10)	0.0145 (11)
Cl1	0.0432 (3)	0.0385 (3)	0.0590 (4)	0.000	−0.0009 (3)	0.000
Cl2	0.0602 (5)	0.1460 (10)	0.0868 (7)	0.000	0.0281 (5)	0.000
N1	0.0406 (11)	0.0353 (10)	0.0402 (11)	0.000	−0.0047 (9)	0.000
O1	0.0623 (12)	0.0639 (13)	0.0371 (10)	0.000	−0.0077 (9)	0.000
O2	0.0505 (8)	0.0460 (8)	0.0615 (8)	0.0089 (6)	−0.0078 (6)	0.0064 (6)
O3	0.0491 (7)	0.0395 (7)	0.0549 (8)	−0.0047 (5)	−0.0017 (6)	0.0056 (6)
O4	0.0579 (11)	0.0386 (10)	0.0402 (9)	0.000	−0.0079 (8)	0.000
O5	0.0794 (11)	0.0744 (12)	0.1034 (13)	0.0009 (9)	−0.0148 (10)	0.0373 (10)
O6	0.0463 (11)	0.0551 (12)	0.0807 (14)	0.000	−0.0060 (10)	0.000
O7	0.0584 (13)	0.0833 (16)	0.0807 (15)	0.000	0.0156 (12)	0.000

Geometric parameters (Å, º)

C1—C2	1.374 (3)	C8—O2	1.426 (2)
C1—C2^{i}	1.374 (3)	C8—H8A	0.9700
C1—Cl2	1.744 (3)	C8—H8B	0.9700
C2—C3	1.385 (3)	C9—O2	1.422 (2)
C2—H2	0.9300	C9—C10	1.489 (3)
C3—C4	1.377 (2)	C9—H9A	0.9700
C3—H3	0.9300	C9—H9B	0.9700
C4—C3^{i}	1.377 (2)	C10—O1	1.427 (2)
C4—N1	1.461 (3)	C10—H10A	0.9700
C5—O4	1.418 (2)	C10—H10B	0.9700
C5—C6	1.489 (3)	Cl1—O5	1.4284 (16)
C5—H5A	0.9700	Cl1—O5^{i}	1.4284 (16)
C5—H5B	0.9700	Cl1—O6	1.436 (2)
C6—O3	1.423 (2)	Cl1—O7	1.437 (2)
C6—H6A	0.9700	N1—H1A	0.8896
C6—H6B	0.9700	N1—H1B	0.8899
C7—O3	1.428 (2)	N1—H1C	0.8901
C7—C8	1.487 (3)	O1—C10^{i}	1.427 (2)
C7—H7A	0.9700	O4—C5^{i}	1.418 (2)
C7—H7B	0.9700		
C2—C1—C2^{i}	121.7 (3)	C7—C8—H8A	109.9
C2—C1—Cl2	119.15 (13)	O2—C8—H8B	109.9
C2^{i}—C1—Cl2	119.15 (13)	C7—C8—H8B	109.9
C1—C2—C3	119.1 (2)	H8A—C8—H8B	108.3
C1—C2—H2	120.5	O2—C9—C10	108.79 (17)
C3—C2—H2	120.5	O2—C9—H9A	109.9
C4—C3—C2	119.59 (19)	C10—C9—H9A	109.9
C4—C3—H3	120.2	O2—C9—H9B	109.9
C2—C3—H3	120.2	C10—C9—H9B	109.9
C3^{i}—C4—C3	120.9 (2)	H9A—C9—H9B	108.3
C3^{i}—C4—N1	119.52 (12)	O1—C10—C9	109.65 (16)
C3—C4—N1	119.52 (12)	O1—C10—H10A	109.7
O4—C5—C6	108.56 (15)	C9—C10—H10A	109.7
O4—C5—H5A	110.0	O1—C10—H10B	109.7
C6—C5—H5A	110.0	C9—C10—H10B	109.7
O4—C5—H5B	110.0	H10A—C10—H10B	108.2
C6—C5—H5B	110.0	O5—Cl1—O5^{i}	110.74 (17)
H5A—C5—H5B	108.4	O5—Cl1—O6	109.74 (9)
O3—C6—C5	109.35 (15)	O5^{i}—Cl1—O6	109.74 (9)
O3—C6—H6A	109.8	O5—Cl1—O7	109.15 (10)
C5—C6—H6A	109.8	O5^{i}—Cl1—O7	109.15 (10)
O3—C6—H6B	109.8	O6—Cl1—O7	108.27 (14)
C5—C6—H6B	109.8	C4—N1—H1A	109.4
H6A—C6—H6B	108.3	C4—N1—H1B	109.5
O3—C7—C8	109.26 (15)	H1A—N1—H1B	109.5

O3—C7—H7A	109.8	C4—N1—H1C	109.5
C8—C7—H7A	109.8	H1A—N1—H1C	109.5
O3—C7—H7B	109.8	H1B—N1—H1C	109.5
C8—C7—H7B	109.8	C10—O1—C10^{i}	112.8 (2)
H7A—C7—H7B	108.3	C9—O2—C8	113.21 (15)
O2—C8—C7	108.89 (15)	C6—O3—C7	111.95 (14)
O2—C8—H8A	109.9	C5—O4—C5^{i}	112.76 (19)
C2^{i}—C1—C2—C3	−0.6 (4)	O2—C9—C10—O1	−65.6 (2)
Cl2—C1—C2—C3	179.84 (17)	C9—C10—O1—C10^{i}	175.35 (13)
C1—C2—C3—C4	0.4 (3)	C10—C9—O2—C8	−168.13 (16)
C2—C3—C4—C3^{i}	−0.3 (4)	C7—C8—O2—C9	−179.95 (16)
C2—C3—C4—N1	−179.03 (18)	C5—C6—O3—C7	171.17 (16)
O4—C5—C6—O3	−66.0 (2)	C8—C7—O3—C6	177.55 (16)
O3—C7—C8—O2	65.9 (2)	C6—C5—O4—C5^{i}	−172.01 (12)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O4	0.89	2.14	2.896 (3)	142
N1—H1*A*···O3^{i}	0.89	2.21	2.9311 (17)	138
N1—H1*B*···O2^{i}	0.89	2.14	2.8952 (18)	143
N1—H1*B*···O1	0.89	2.18	2.870 (3)	134
N1—H1*C*···O2	0.89	2.15	2.8952 (18)	140
N1—H1*C*···O3	0.89	2.20	2.9311 (17)	139

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