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A triclinic polymorph of 4-cyanopyridinium hydrogen chloranilate

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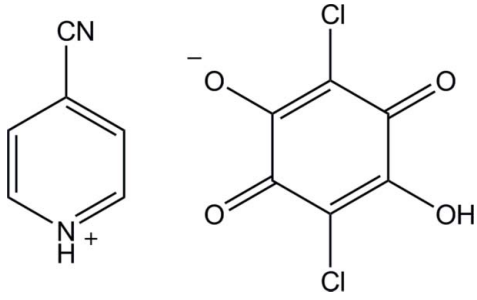
Key indicators: single-crystal X-ray study; T = 180 K; mean σ(C–C) = 0.003 Å; R factor = 0.066; wR factor = 0.164; data-to-parameter ratio = 18.9.

The asymmetric unit of the triclinic polymorph of the title compound (systematic name: 4-cyanopyridinium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate), $C_6H_5N_2^+\cdot C_6HCl_2O_4^-$, consists of two crystallographically independent cation–anion units, in each of which the cation and the anion are linked by an N—H···O hydrogen bond. In the units, the dihedral angles between the cation and anion rings are 78.43 (11) and 80.71 (11)°. In the crystal, each unit independently forms a chain through N—H···O and O—H···N hydrogen bonds; one chain runs along the c axis while the other runs along [011]. Weak C—H···O, C—H···N and C—H···Cl interactions are observed between the chains.

Related literature

For the monoclinic polymorph, see: Tomura & Yamashita (2008); Gotoh *et al.* (2008). For hydrogen-bonding patterns in chloranilic acid–organic base (1/1) systems, see: Ishida & Kashino (2002). For ^{35}Cl nuclear quadrupole resonance studies on proton transfer in chloranilic acid–organic base systems, see: Nihei *et al.* (2000).



Experimental

Crystal data

$C_6H_5N_2^+\cdot C_6HCl_2O_4^-$
M_r = 313.10
Triclinic, $P\overline{1}$
a = 9.3918 (7) Å
b = 10.6652 (7) Å
c = 13.9135 (8) Å
α = 111.8033 (18)°
β = 106.258 (3)°
γ = 90.416 (3)°
V = 1232.50 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.54 mm^{-1}
T = 180 K
0.36 × 0.31 × 0.09 mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.866, T_{max} = 0.953
21354 measured reflections
7135 independent reflections
4934 reflections with $I > 2\sigma(I)$
R_{int} = 0.108

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.164
S = 0.99
7135 reflections
377 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.95 (4)	1.67 (4)	2.602 (2)	170 (3)
N3—H3···O6	0.90 (4)	1.84 (4)	2.719 (3)	166 (3)
O4—H4···N2^{i}	0.80 (4)	1.99 (4)	2.741 (3)	155 (4)
O8—H8···N4^{ii}	0.93 (5)	2.07 (5)	2.875 (3)	144 (4)
C13—H13···N4^{iii}	0.95	2.55	3.407 (3)	150
C14—H14···O3^{iv}	0.95	2.42	3.209 (3)	141
C16—H16···Cl3^{v}	0.95	2.71	3.431 (3)	133
C17—H17···O1^{vi}	0.95	2.30	3.194 (3)	157
C19—H19···O2	0.95	2.25	3.192 (3)	170
C20—H20···Cl1	0.95	2.83	3.626 (3)	142
C23—H23···O5^{vii}	0.95	2.14	3.040 (3)	158

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

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: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5521).

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supporting information

Acta Cryst. (2012). E**68**, o2830 [https://doi.org/10.1107/S1600536812037221]

A triclinic polymorph of 4-cyanopyridinium hydrogen chloranilate

Kazuma Gotoh and Hiroyuki Ishida

S1. Comment

The title compound was accidentally obtained in the preparation of the monoclinic polymorph of 4-cyanopyridinium chloranilate, $C_6H_5N_2^+.C_6HCl_2O_4^-$, which is an interesting model compound for investigating proton transfer in the hydrogen bond systems (Nihei *et al.*, 2000). The structure of the monoclinic polymorph has been reported by Tomura & Yamashita (2008) and Gotoh *et al.* (2008).

The asymmetric unit of the triclinic polymorph of the title compound consists of two crystallographically independent cation–anion units, in each of which the cation and the anion are held together by N—H···O hydrogen bond. The dihedral angle between the N1/C13–C17 pyridine ring and the C1–C6 of the acid ring is 78.43 (11)° in one unit, while the angle between the N3/C19–C23 and C7–C12 rings is 80.71 (11)° in the other unit.

In the crystal structure of the monoclinic polymorph, the acid molecule (A) and the base molecule (B) afford an centrosymmetric 2:2 (B:A:A:B) aggregate (Ishida & Kashino, 2002) through O—H···O and N···H···O hydrogen bonds and the H atom in the N···H···O hydrogen bond is disordered over two positions (Gotoh *et al.*, 2008). In contrast to the monoclinic form, the present triclinic polymorph shows two crystallographically independent 1:1 (A:B) units of the acid and base molecules. Each unit independently forms a hydrogen-bonded (–A:B:A:B–) chain; one chain formed by N1—H1···O2 and O4—H4···N2^{i} (symmetry code in Table 1) hydrogen bonds runs along the *c* axis, while the other chain formed by N3—H3···O6 and O8—H8···N4^{ii} (symmetry code in Table 1) hydrogen bonds runs along the [011] direction. No H atom disorder is observed in these hydrogen bonds. Between the chains, C—H···O, C—H···N and C—H···Cl interactions (Table 1) are observed.

S2. Experimental

Single crystals were obtained by slow evaporation from an acetonitrile solution (130 ml) of chloranilic acid (0.60 g) and 4-cyanopyridine (0.30 g) at room temperature.

S3. Refinement

C-bound H atoms were positioned geometrically (C—H = 0.95 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). The O– and N-bound H atoms were found in a difference Fourier map and refined freely. The refined distances are O—H = 0.80 (4) and 0.93 (5) Å, and N—H = 0.90 (4) and 0.95 (4) Å.

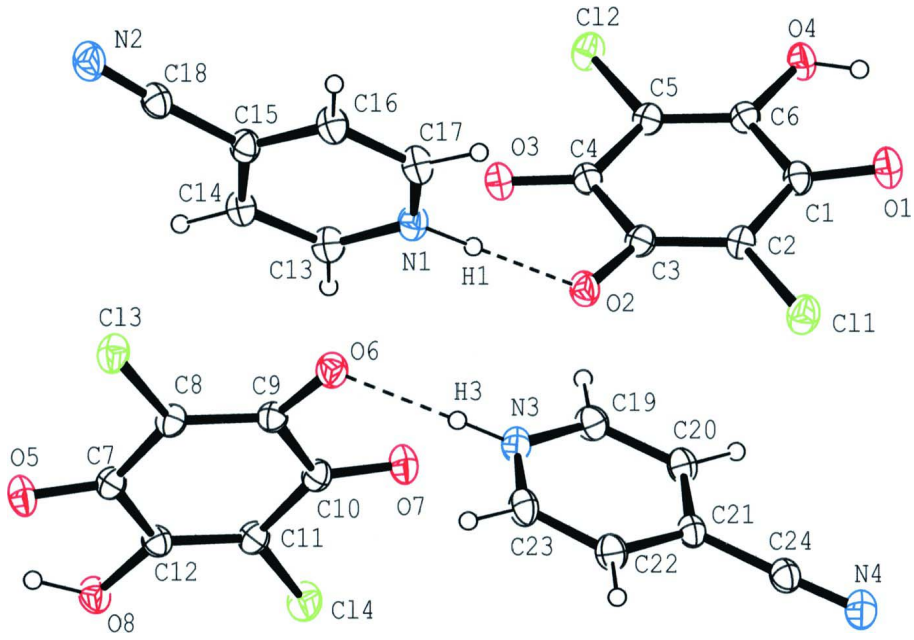

Figure 1

The asymmetric unit of the title compound, with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. The dashed lines indicate the N—H···O hydrogen bonds.

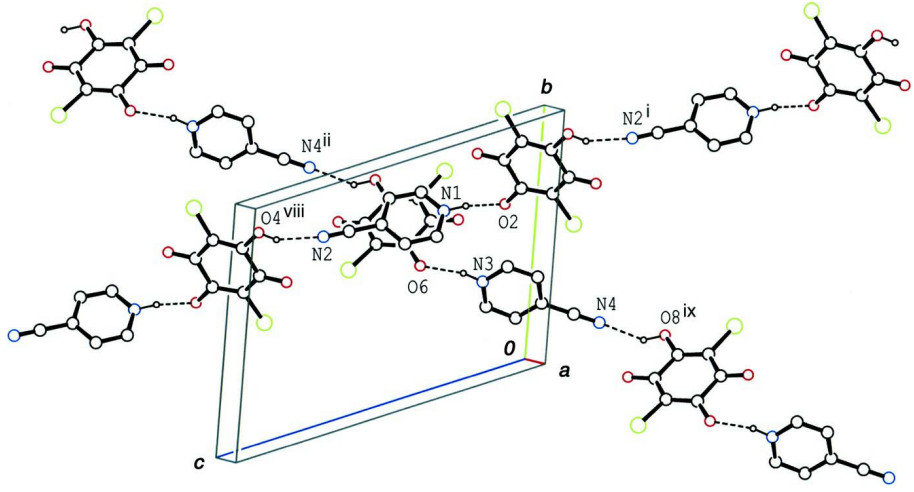

Figure 2

A packing diagram of the title compound, showing two crystallographically independent chains formed by N—H···O and O—H···N hydrogen bonds (dashed lines). H atoms not involved in the hydrogen bonds have been omitted. [Symmetry codes: (i) *x*, *y*, *z* - 1; (ii) *x*, *y* + 1, *z* + 1; (viii) *x*, *y*, *z* + 1; (ix) *x*, *y* - 1, *z* - 1.]

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

Crystal data

$C_6H_5N_2^+·C_6HCl_2O_4^-$
M_r = 313.10
Triclinic, $P\overline{1}$
Hall symbol: -P 1

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b = 10.6652 (7) Å
c = 13.9135 (8) Å
α = 111.8033 (18)°

β = 106.258 (3)°
γ = 90.416 (3)°
V = 1232.50 (14) Å^3
Z = 4
F(000) = 632.00
D_x = 1.687 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å

Cell parameters from 17217 reflections
θ = 3.1–30.1°
μ = 0.54 mm^{-1}
T = 180 K
Platelet, brown
0.36 × 0.31 × 0.09 mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.866, T_{max} = 0.953
21354 measured reflections

7135 independent reflections
4934 reflections with $I > 2\sigma(I)$
R_{int} = 0.108
θ_{max} = 30.0°
h = −13→13
k = −14→14
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.164
S = 0.99
7135 reflections
377 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
$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 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	0.29193 (7)	0.49544 (6)	−0.10659 (5)	0.04057 (16)
Cl2	0.68163 (7)	1.06889 (5)	0.18401 (5)	0.03666 (15)
Cl3	0.21149 (7)	0.59716 (6)	0.62343 (5)	0.03851 (16)
Cl4	−0.16421 (7)	0.85552 (7)	0.30375 (5)	0.04279 (17)
O1	0.51735 (19)	0.64141 (17)	−0.15370 (13)	0.0396 (4)
O2	0.32328 (17)	0.66708 (16)	0.12870 (12)	0.0346 (3)
O3	0.48242 (18)	0.91360 (17)	0.24401 (13)	0.0363 (4)
O4	0.67459 (19)	0.88479 (17)	−0.03878 (14)	0.0343 (4)
O5	−0.01092 (19)	0.79448 (17)	0.65480 (13)	0.0384 (4)
O6	0.19311 (18)	0.52007 (16)	0.38448 (13)	0.0364 (4)

O7	0.04975 (18)	0.65162 (17)	0.26162 (13)	0.0370 (4)
O8	−0.16121 (19)	0.90831 (17)	0.53085 (14)	0.0376 (4)
N1	0.4187 (2)	0.7224 (2)	0.33632 (16)	0.0344 (4)
N2	0.6554 (2)	0.7841 (2)	0.74522 (17)	0.0424 (5)
N3	0.0861 (2)	0.3707 (2)	0.16703 (16)	0.0341 (4)
N4	−0.1526 (2)	0.0443 (2)	−0.24595 (17)	0.0413 (5)
C1	0.4981 (2)	0.7009 (2)	−0.06484 (17)	0.0298 (4)
C2	0.3989 (2)	0.6506 (2)	−0.02287 (17)	0.0302 (4)
C3	0.3974 (2)	0.7129 (2)	0.08301 (17)	0.0296 (4)
C4	0.4895 (2)	0.8540 (2)	0.15269 (17)	0.0289 (4)
C5	0.5819 (2)	0.9100 (2)	0.10598 (17)	0.0296 (4)
C6	0.5880 (2)	0.8389 (2)	0.00544 (17)	0.0292 (4)
C7	0.0119 (2)	0.7548 (2)	0.56596 (17)	0.0301 (4)
C8	0.1100 (2)	0.6605 (2)	0.53026 (18)	0.0306 (4)
C9	0.1187 (2)	0.6129 (2)	0.42538 (17)	0.0292 (4)
C10	0.0303 (2)	0.6811 (2)	0.35009 (17)	0.0305 (4)
C11	−0.0679 (2)	0.7803 (2)	0.38836 (18)	0.0319 (4)
C12	−0.0762 (2)	0.8166 (2)	0.48929 (18)	0.0301 (4)
C13	0.3814 (3)	0.8248 (2)	0.41276 (19)	0.0354 (5)
H13	0.3173	0.8851	0.3923	0.042*
C14	0.4348 (3)	0.8434 (2)	0.52031 (19)	0.0338 (5)
H14	0.4081	0.9150	0.5750	0.041*
C15	0.5302 (3)	0.7526 (2)	0.54595 (18)	0.0321 (4)
C16	0.5662 (3)	0.6461 (2)	0.46590 (19)	0.0378 (5)
H16	0.6298	0.5841	0.4839	0.045*
C17	0.5075 (3)	0.6327 (2)	0.3596 (2)	0.0381 (5)
H17	0.5296	0.5603	0.3030	0.046*
C18	0.5972 (3)	0.7707 (2)	0.65759 (19)	0.0357 (5)
C19	0.1208 (3)	0.4009 (2)	0.09031 (19)	0.0359 (5)
H19	0.1878	0.4798	0.1103	0.043*
C20	0.0589 (3)	0.3172 (2)	−0.01748 (18)	0.0342 (5)
H20	0.0824	0.3372	−0.0728	0.041*
C21	−0.0390 (2)	0.2024 (2)	−0.04369 (17)	0.0303 (4)
C22	−0.0737 (3)	0.1742 (2)	0.03736 (19)	0.0355 (5)
H22	−0.1409	0.0965	0.0200	0.043*
C23	−0.0083 (3)	0.2619 (2)	0.14348 (19)	0.0363 (5)
H23	−0.0304	0.2448	0.2004	0.044*
C24	−0.1034 (3)	0.1137 (2)	−0.15641 (18)	0.0340 (5)
H1	0.384 (3)	0.713 (3)	0.263 (3)	0.063 (9)*
H3	0.121 (3)	0.432 (3)	0.236 (3)	0.056 (9)*
H4	0.665 (4)	0.833 (4)	−0.100 (3)	0.068 (11)*
H8	−0.140 (4)	0.918 (4)	0.603 (4)	0.097 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0498 (4)	0.0352 (3)	0.0327 (3)	−0.0051 (3)	0.0117 (3)	0.0097 (2)
Cl2	0.0453 (3)	0.0310 (3)	0.0314 (3)	−0.0010 (2)	0.0092 (2)	0.0116 (2)

Cl3	0.0490 (3)	0.0387 (3)	0.0311 (3)	0.0160 (3)	0.0107 (3)	0.0180 (2)
Cl4	0.0500 (4)	0.0509 (4)	0.0361 (3)	0.0186 (3)	0.0126 (3)	0.0265 (3)
O1	0.0532 (10)	0.0367 (9)	0.0316 (8)	0.0031 (8)	0.0210 (8)	0.0102 (7)
O2	0.0398 (9)	0.0382 (8)	0.0290 (8)	0.0011 (7)	0.0142 (7)	0.0139 (7)
O3	0.0433 (9)	0.0379 (8)	0.0292 (8)	0.0064 (7)	0.0169 (7)	0.0104 (7)
O4	0.0431 (9)	0.0355 (8)	0.0282 (8)	0.0033 (7)	0.0172 (7)	0.0119 (7)
O5	0.0533 (10)	0.0417 (9)	0.0305 (8)	0.0177 (8)	0.0226 (8)	0.0181 (7)
O6	0.0396 (9)	0.0368 (8)	0.0322 (8)	0.0112 (7)	0.0112 (7)	0.0123 (7)
O7	0.0490 (10)	0.0388 (9)	0.0289 (8)	0.0111 (7)	0.0183 (7)	0.0145 (7)
O8	0.0428 (9)	0.0399 (9)	0.0348 (9)	0.0173 (7)	0.0156 (8)	0.0168 (8)
N1	0.0418 (11)	0.0349 (9)	0.0277 (9)	0.0021 (8)	0.0118 (8)	0.0127 (8)
N2	0.0492 (12)	0.0501 (12)	0.0346 (10)	0.0079 (10)	0.0168 (10)	0.0210 (10)
N3	0.0393 (10)	0.0356 (10)	0.0286 (9)	0.0110 (8)	0.0114 (9)	0.0127 (9)
N4	0.0495 (12)	0.0425 (11)	0.0331 (10)	0.0096 (9)	0.0152 (10)	0.0139 (9)
C1	0.0364 (11)	0.0292 (10)	0.0274 (10)	0.0085 (9)	0.0120 (9)	0.0132 (9)
C2	0.0349 (11)	0.0279 (10)	0.0267 (10)	0.0035 (9)	0.0089 (9)	0.0099 (9)
C3	0.0318 (11)	0.0303 (10)	0.0281 (10)	0.0046 (8)	0.0080 (9)	0.0135 (9)
C4	0.0317 (10)	0.0310 (10)	0.0277 (10)	0.0094 (9)	0.0111 (9)	0.0138 (9)
C5	0.0326 (11)	0.0284 (10)	0.0286 (10)	0.0042 (8)	0.0088 (9)	0.0123 (9)
C6	0.0316 (10)	0.0303 (10)	0.0288 (10)	0.0059 (8)	0.0093 (9)	0.0148 (9)
C7	0.0332 (11)	0.0297 (10)	0.0286 (10)	0.0038 (9)	0.0080 (9)	0.0138 (9)
C8	0.0345 (11)	0.0304 (10)	0.0289 (10)	0.0070 (9)	0.0073 (9)	0.0153 (9)
C9	0.0299 (10)	0.0291 (10)	0.0288 (10)	0.0049 (8)	0.0084 (9)	0.0118 (9)
C10	0.0331 (11)	0.0312 (10)	0.0278 (10)	0.0026 (9)	0.0081 (9)	0.0129 (9)
C11	0.0346 (11)	0.0355 (11)	0.0291 (10)	0.0064 (9)	0.0078 (9)	0.0177 (9)
C12	0.0315 (11)	0.0293 (10)	0.0315 (11)	0.0068 (9)	0.0113 (9)	0.0127 (9)
C13	0.0405 (12)	0.0333 (11)	0.0360 (12)	0.0060 (10)	0.0126 (10)	0.0166 (10)
C14	0.0408 (12)	0.0313 (10)	0.0313 (10)	0.0069 (9)	0.0149 (10)	0.0114 (9)
C15	0.0367 (11)	0.0345 (11)	0.0284 (10)	0.0023 (9)	0.0116 (9)	0.0147 (9)
C16	0.0463 (13)	0.0356 (11)	0.0362 (12)	0.0108 (10)	0.0175 (11)	0.0155 (10)
C17	0.0472 (13)	0.0363 (12)	0.0346 (11)	0.0093 (10)	0.0193 (11)	0.0128 (10)
C18	0.0407 (12)	0.0390 (12)	0.0338 (11)	0.0078 (10)	0.0166 (10)	0.0173 (10)
C19	0.0383 (12)	0.0352 (11)	0.0371 (12)	0.0039 (9)	0.0138 (10)	0.0158 (10)
C20	0.0409 (12)	0.0360 (11)	0.0313 (11)	0.0061 (10)	0.0159 (10)	0.0156 (10)
C21	0.0354 (11)	0.0322 (10)	0.0276 (10)	0.0093 (9)	0.0133 (9)	0.0136 (9)
C22	0.0435 (13)	0.0348 (11)	0.0346 (11)	0.0047 (10)	0.0162 (10)	0.0172 (10)
C23	0.0465 (13)	0.0400 (12)	0.0311 (11)	0.0113 (10)	0.0170 (10)	0.0194 (10)
C24	0.0373 (12)	0.0378 (11)	0.0317 (11)	0.0083 (10)	0.0140 (10)	0.0160 (10)

Geometric parameters (Å, º)

Cl1—C2	1.730 (2)	C4—C5	1.460 (3)
Cl2—C5	1.722 (2)	C5—C6	1.339 (3)
Cl3—C8	1.736 (2)	C7—C8	1.416 (3)
Cl4—C11	1.721 (2)	C7—C12	1.514 (3)
O1—C1	1.228 (3)	C8—C9	1.382 (3)
O2—C3	1.265 (2)	C9—C10	1.551 (3)
O3—C4	1.213 (2)	C10—C11	1.457 (3)

O4—C6	1.333 (2)	C11—C12	1.336 (3)
O4—H4	0.80 (4)	C13—C14	1.374 (3)
O5—C7	1.231 (2)	C13—H13	0.9500
O6—C9	1.267 (3)	C14—C15	1.399 (3)
O7—C10	1.219 (2)	C14—H14	0.9500
O8—C12	1.334 (3)	C15—C16	1.386 (3)
O8—H8	0.93 (4)	C15—C18	1.440 (3)
N1—C13	1.341 (3)	C16—C17	1.377 (3)
N1—C17	1.344 (3)	C16—H16	0.9500
N1—H1	0.95 (3)	C17—H17	0.9500
N2—C18	1.141 (3)	C19—C20	1.376 (3)
N3—C23	1.334 (3)	C19—H19	0.9500
N3—C19	1.341 (3)	C20—C21	1.393 (3)
N3—H3	0.90 (3)	C20—H20	0.9500
N4—C24	1.141 (3)	C21—C22	1.387 (3)
C1—C2	1.424 (3)	C21—C24	1.442 (3)
C1—C6	1.512 (3)	C22—C23	1.375 (3)
C2—C3	1.377 (3)	C22—H22	0.9500
C3—C4	1.543 (3)	C23—H23	0.9500

C6—O4—H4	111 (2)	C12—C11—C10	120.14 (19)
C12—O8—H8	105 (2)	C12—C11—Cl4	121.12 (18)
C13—N1—C17	122.6 (2)	C10—C11—Cl4	118.65 (16)
C13—N1—H1	120 (2)	O8—C12—C11	123.68 (19)
C17—N1—H1	118 (2)	O8—C12—C7	114.58 (18)
C23—N3—C19	122.6 (2)	C11—C12—C7	121.7 (2)
C23—N3—H3	119.4 (19)	N1—C13—C14	120.7 (2)
C19—N3—H3	118 (2)	N1—C13—H13	119.6
O1—C1—C2	125.5 (2)	C14—C13—H13	119.6
O1—C1—C6	116.86 (18)	C13—C14—C15	117.2 (2)
C2—C1—C6	117.66 (19)	C13—C14—H14	121.4
C3—C2—C1	122.6 (2)	C15—C14—H14	121.4
C3—C2—Cl1	120.10 (16)	C16—C15—C14	121.4 (2)
C1—C2—Cl1	116.92 (17)	C16—C15—C18	118.3 (2)
O2—C3—C2	126.0 (2)	C14—C15—C18	120.2 (2)
O2—C3—C4	115.97 (19)	C17—C16—C15	118.3 (2)
C2—C3—C4	117.96 (18)	C17—C16—H16	120.9
O3—C4—C5	122.7 (2)	C15—C16—H16	120.9
O3—C4—C3	118.70 (18)	N1—C17—C16	119.8 (2)
C5—C4—C3	118.59 (18)	N1—C17—H17	120.1
C6—C5—C4	120.3 (2)	C16—C17—H17	120.1
C6—C5—Cl2	121.68 (16)	N2—C18—C15	177.4 (3)
C4—C5—Cl2	117.99 (16)	N3—C19—C20	119.8 (2)
O4—C6—C5	122.1 (2)	N3—C19—H19	120.1
O4—C6—C1	115.73 (19)	C20—C19—H19	120.1
C5—C6—C1	122.17 (18)	C19—C20—C21	118.5 (2)
O5—C7—C8	127.07 (19)	C19—C20—H20	120.7
O5—C7—C12	114.44 (19)	C21—C20—H20	120.7

C8—C7—C12	118.49 (19)	C22—C21—C20	120.5 (2)
C9—C8—C7	122.90 (18)	C22—C21—C24	120.7 (2)
C9—C8—Cl3	120.81 (16)	C20—C21—C24	118.83 (19)
C7—C8—Cl3	116.14 (16)	C23—C22—C21	118.2 (2)
O6—C9—C8	126.72 (19)	C23—C22—H22	120.9
O6—C9—C10	116.38 (18)	C21—C22—H22	120.9
C8—C9—C10	116.90 (18)	N3—C23—C22	120.4 (2)
O7—C10—C11	122.69 (19)	N3—C23—H23	119.8
O7—C10—C9	117.86 (19)	C22—C23—H23	119.8
C11—C10—C9	119.41 (18)	N4—C24—C21	178.9 (3)

O1—C1—C2—C3	170.6 (2)	O6—C9—C10—O7	−7.3 (3)
C6—C1—C2—C3	−9.2 (3)	C8—C9—C10—O7	171.9 (2)
O1—C1—C2—Cl1	−2.5 (3)	O6—C9—C10—C11	174.71 (19)
C6—C1—C2—Cl1	177.63 (15)	C8—C9—C10—C11	−6.1 (3)
C1—C2—C3—O2	−172.6 (2)	O7—C10—C11—C12	−174.8 (2)
Cl1—C2—C3—O2	0.3 (3)	C9—C10—C11—C12	3.1 (3)
C1—C2—C3—C4	9.6 (3)	O7—C10—C11—Cl4	1.7 (3)
Cl1—C2—C3—C4	−177.44 (15)	C9—C10—C11—Cl4	179.63 (15)
O2—C3—C4—O3	−2.2 (3)	C10—C11—C12—O8	178.7 (2)
C2—C3—C4—O3	175.76 (19)	Cl4—C11—C12—O8	2.3 (3)
O2—C3—C4—C5	177.69 (18)	C10—C11—C12—C7	−1.4 (3)
C2—C3—C4—C5	−4.4 (3)	Cl4—C11—C12—C7	−177.88 (16)
O3—C4—C5—C6	178.8 (2)	O5—C7—C12—O8	2.3 (3)
C3—C4—C5—C6	−1.1 (3)	C8—C7—C12—O8	−177.45 (19)
O3—C4—C5—Cl2	−1.2 (3)	O5—C7—C12—C11	−177.6 (2)
C3—C4—C5—Cl2	178.92 (14)	C8—C7—C12—C11	2.7 (3)
C4—C5—C6—O4	−177.88 (19)	C17—N1—C13—C14	0.8 (3)
Cl2—C5—C6—O4	2.1 (3)	N1—C13—C14—C15	0.7 (3)
C4—C5—C6—C1	1.6 (3)	C13—C14—C15—C16	−1.6 (3)
Cl2—C5—C6—C1	−178.48 (15)	C13—C14—C15—C18	176.4 (2)
O1—C1—C6—O4	2.9 (3)	C14—C15—C16—C17	1.0 (3)
C2—C1—C6—O4	−177.21 (18)	C18—C15—C16—C17	−177.1 (2)
O1—C1—C6—C5	−176.6 (2)	C13—N1—C17—C16	−1.4 (3)
C2—C1—C6—C5	3.3 (3)	C15—C16—C17—N1	0.5 (3)
O5—C7—C8—C9	174.2 (2)	C23—N3—C19—C20	−0.5 (3)
C12—C7—C8—C9	−6.1 (3)	N3—C19—C20—C21	0.0 (3)
O5—C7—C8—Cl3	−1.5 (3)	C19—C20—C21—C22	0.5 (3)
C12—C7—C8—Cl3	178.26 (15)	C19—C20—C21—C24	−179.5 (2)
C7—C8—C9—O6	−173.2 (2)	C20—C21—C22—C23	−0.4 (3)
Cl3—C8—C9—O6	2.2 (3)	C24—C21—C22—C23	179.6 (2)
C7—C8—C9—C10	7.6 (3)	C19—N3—C23—C22	0.6 (3)
Cl3—C8—C9—C10	−176.91 (15)	C21—C22—C23—N3	−0.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.95 (4)	1.67 (4)	2.602 (2)	170 (3)

N3—H3···O6	0.90 (4)	1.84 (4)	2.719 (3)	166 (3)
O4—H4···N2^{i}	0.80 (4)	1.99 (4)	2.741 (3)	155 (4)
O8—H8···N4^{ii}	0.93 (5)	2.07 (5)	2.875 (3)	144 (4)
C13—H13···N4^{iii}	0.95	2.55	3.407 (3)	150
C14—H14···O3^{iv}	0.95	2.42	3.209 (3)	141
C16—H16···Cl3^{v}	0.95	2.71	3.431 (3)	133
C17—H17···O1^{vi}	0.95	2.30	3.194 (3)	157
C19—H19···O2	0.95	2.25	3.192 (3)	170
C20—H20···Cl1	0.95	2.83	3.626 (3)	142
C23—H23···O5^{vii}	0.95	2.14	3.040 (3)	158

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