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4-Aminopyridinium 2-chloro-4-nitrobenzoate monohydrate

Kelsey L. Savig and Andreas Lemmerer*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, PO Wits 2050, South Africa
Correspondence e-mail: andreas.lemmerer@wits.ac.za

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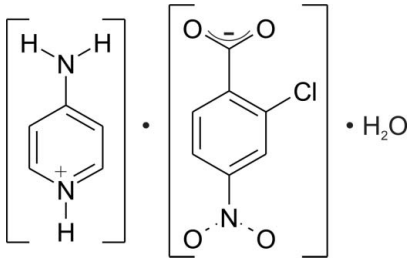
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.122; data-to-parameter ratio = 16.5.

In the title hydrated molecular salt, $C_5H_7N_2^+\cdot C_7H_3ClNO_4^-\cdot H_2O$, the ions and water molecules assemble into ribbons of $R_6^5(22)$ rings along the c axis *via* O(water)—H···O$^-$, N$^+$—H···O(water) and N—H···O$^-$ hydrogen bonds. N—H···O$^-$ hydrogen bonds connect adjacent ribbons along the c-axis direction *via* $R_4^4(12)$ rings, forming hydrogen-bonded layers. The CO_2 and NO_2 groups make dihedral angles of 81.8 (2) and 1.4 (2)°, respectively, with the ring in the anion.

Related literature

For related structures, see: Lemmerer *et al.* (2010). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_5H_7N_2^+\cdot C_7H_3ClNO_4^-\cdot H_2O$
M_r = 313.7
Monoclinic, $P2_1/c$
a = 14.4500 (5) Å
b = 14.3300 (5) Å
c = 6.9918 (2) Å
β = 97.804 (2)°
V = 1434.37 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 173 K
0.78 × 0.31 × 0.09 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 2004)
T_{min} = 0.896, T_{max} = 0.977
14928 measured reflections
3456 independent reflections
2685 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.122
S = 1.04
3456 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.5 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
N2—H2···O1W^{i}	0.93 (3)	1.72 (3)	2.641 (2)	170 (2)
N3—H3A···O1	0.94 (2)	1.99 (2)	2.926 (2)	171.1 (19)
N3—H3B···O2^{ii}	0.84 (2)	2.16 (3)	2.982 (2)	165 (2)
O1W—H1W···O1^{iii}	0.75 (3)	1.96 (3)	2.698 (2)	166 (3)
O1W—H2W···O2	0.78 (4)	1.99 (4)	2.729 (2)	158 (3)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2073).

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4-Aminopyridinium 2-chloro-4-nitrobenzoate monohydrate

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S1. Comment

The title molecular salt is part of a larger research project looking at the factors that determine if a salt or a co-crystal forms between a specific carboxylic acid and various pyridine ring systems (Lemmerer *et al.*, 2010).

In molecular salt (I) (Fig. 1), formed by dissolving 4-aminopyridine and 2-chloro-4-nitrobenzoic acid in methanol, two kinds of hydrogen-bonded rings are formed. The ring $R^5_6(22)$ (Bernstein *et al.*, 1995) uses O1W—H···O^-, N^+—H···O and N—H···O^- hydrogen bonds to connect all three species together into a 1-D ribbon (Fig. 2) along the *c*-axis. In addition, a $R^4_4(12)$ ring is formed between two amine groups and two carboxylate groups to connect two ribbons together to form layers (Fig. 3).

S2. Experimental

Crystals were grown by slow evaporation of a methanol solution of 2-chloro-4-nitrobenzoic acid (0.100 g; 0.496 mmol) and 4-aminopyridine (0.047 g; 0.50 mmol) in 8 ml of methanol, and afforded colourless plates after three days of slow evaporation at ambient conditions.

S3. Refinement

The aromatic C-bound H atoms were geometrically placed with C—H bond lengths of 0.95 Å, and were refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atoms of the water molecule and the N-bound H atoms were located in the difference map and their coordinates as well as isotropic displacement parameters were refined freely. The residual electron density around the O atom of the water molecule was found to not correspond to any H atoms by inspection of the hydrogen bonding geometry.

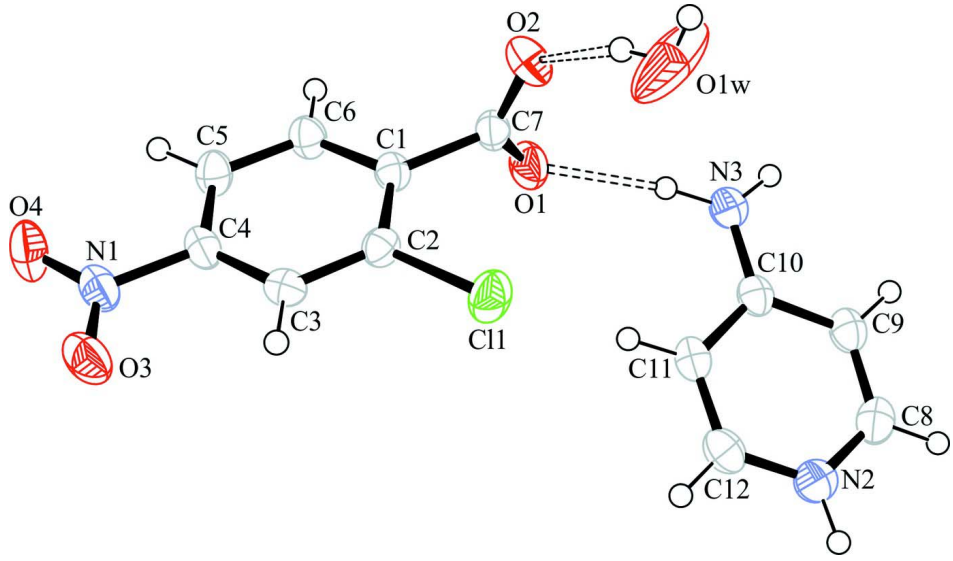

Figure 1

The asymmetric unit of (I) showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

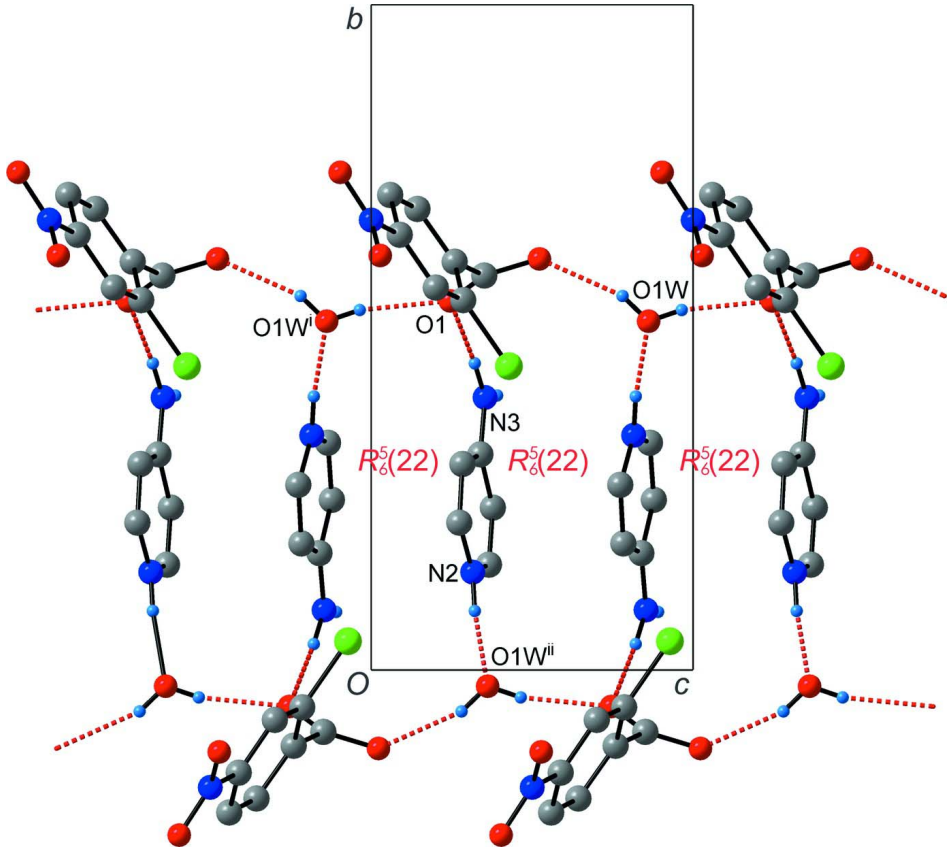

Figure 2

Hydrogen bonding diagram of (I) showing the $R^5_6(22)$ rings to form ribbons. Intermolecular hydrogen bonds are shown as dashed red lines forming dimers. Atoms with superscrips (i) and (ii) are at the symmetry positions (x, y, z - 1) and (x, -y + 1/2, z - 1/2) respectively.

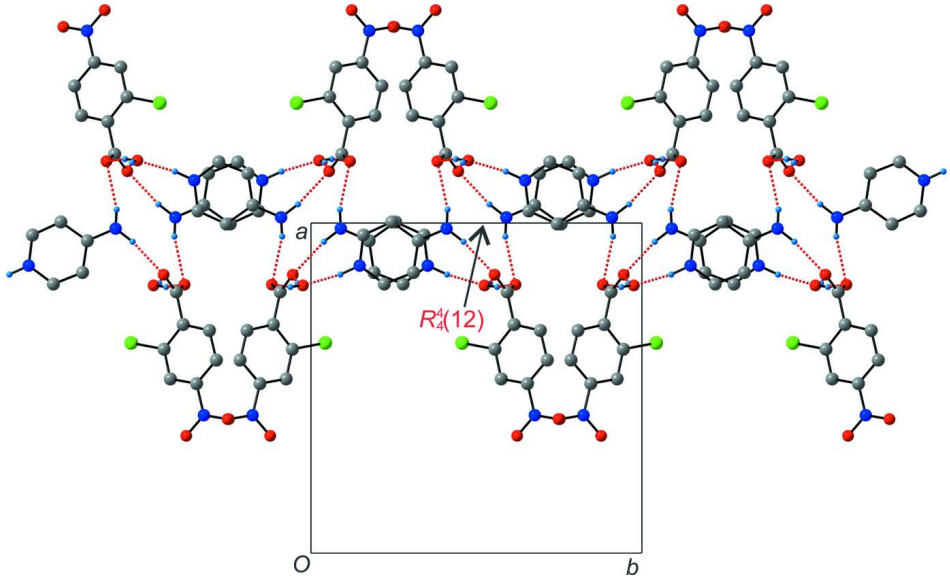

Figure 3

The layers form by combining the one-dimensional ribbons using $R^4_4(12)$ rings.

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Crystal data

$C_5H_7N_2^+·C_7H_3ClNO_4^-·H_2O$
M_r = 313.7
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 14.4500 (5) Å
b = 14.3300 (5) Å
c = 6.9918 (2) Å
β = 97.804 (2)°
V = 1434.37 (8) Å^3
Z = 4
$F(000)$ = 648
D_x = 1.453 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4262 reflections
θ = 2.8–27.8°
μ = 0.29 mm^{-1}
T = 173 K
Plate, colourless
0.78 × 0.31 × 0.09 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
ω scans
Absorption correction: integration (*XPREP*; Bruker, 2004)
T_{min} = 0.896, T_{max} = 0.977
14928 measured reflections
3456 independent reflections
2685 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 28°, θ_{min} = 1.4°
h = −19→19
k = −18→18
l = −8→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.122
S = 1.04
3456 reflections
210 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.1397P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.5 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

Experimental. Numerical integration absorption corrections based on indexed crystal faces were applied using the *XPREP* routine (Bruker, 2004)

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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.69246 (11)	0.61389 (11)	0.2594 (2)	0.0261 (3)
C2	0.61757 (12)	0.55610 (11)	0.2858 (2)	0.0271 (3)
C3	0.52758 (11)	0.57500 (11)	0.2008 (2)	0.0284 (3)
H3	0.4772	0.5348	0.2188	0.034*
C4	0.51347 (11)	0.65438 (12)	0.0887 (2)	0.0290 (4)
C5	0.58469 (12)	0.71419 (12)	0.0592 (2)	0.0325 (4)

H5	0.5725	0.7687	−0.0176	0.039*
C6	0.67437 (12)	0.69317 (12)	0.1438 (2)	0.0311 (4)
H6	0.7245	0.7332	0.1232	0.037*
C7	0.79130 (11)	0.59307 (11)	0.3515 (2)	0.0291 (3)
N1	0.41775 (10)	0.67644 (11)	0.0004 (2)	0.0349 (3)
O1	0.84325 (9)	0.55490 (9)	0.24589 (19)	0.0412 (3)
O2	0.81313 (9)	0.61801 (10)	0.52270 (17)	0.0424 (3)
O3	0.35519 (9)	0.62315 (10)	0.0282 (2)	0.0462 (3)
O4	0.40575 (10)	0.74821 (11)	−0.0962 (2)	0.0513 (4)
Cl1	0.63660 (3)	0.45679 (3)	0.42817 (7)	0.04119 (15)
C8	0.96351 (14)	0.15836 (13)	0.3659 (2)	0.0361 (4)
H8	1.0019	0.1049	0.3936	0.043*
C9	1.00312 (12)	0.24412 (13)	0.3780 (2)	0.0341 (4)
H9	1.0687	0.2506	0.4123	0.041*
C10	0.94613 (12)	0.32426 (12)	0.3393 (2)	0.0293 (4)
C11	0.84995 (12)	0.30971 (12)	0.2835 (2)	0.0309 (4)
H11	0.8095	0.3614	0.2527	0.037*
C12	0.81509 (13)	0.22161 (13)	0.2739 (2)	0.0352 (4)
H12	0.75	0.2124	0.237	0.042*
N2	0.87086 (12)	0.14714 (11)	0.3155 (2)	0.0357 (3)
N3	0.98294 (12)	0.40973 (11)	0.3540 (2)	0.0368 (4)
H2	0.8439 (17)	0.0887 (18)	0.322 (3)	0.061 (7)*
H3A	0.9432 (16)	0.4610 (15)	0.322 (3)	0.045 (6)*
H3B	1.0408 (17)	0.4127 (15)	0.391 (3)	0.048 (6)*
O1W	0.8108 (2)	0.52435 (14)	0.8618 (3)	0.1094 (11)
H1W	0.817 (2)	0.541 (2)	0.965 (5)	0.080 (10)*
H2W	0.806 (2)	0.562 (2)	0.781 (5)	0.096 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0257 (8)	0.0296 (8)	0.0228 (7)	0.0026 (6)	0.0032 (6)	−0.0001 (6)
C2	0.0310 (8)	0.0261 (8)	0.0245 (7)	0.0017 (6)	0.0048 (6)	0.0017 (6)
C3	0.0268 (8)	0.0306 (8)	0.0281 (8)	−0.0034 (6)	0.0046 (6)	−0.0036 (6)
C4	0.0241 (8)	0.0377 (9)	0.0244 (7)	0.0046 (6)	0.0007 (6)	−0.0018 (6)
C5	0.0319 (9)	0.0339 (9)	0.0312 (8)	0.0036 (7)	0.0030 (7)	0.0082 (7)
C6	0.0265 (9)	0.0340 (9)	0.0325 (8)	−0.0007 (7)	0.0033 (6)	0.0062 (7)
C7	0.0260 (8)	0.0281 (8)	0.0319 (8)	0.0004 (6)	−0.0007 (6)	0.0059 (6)
N1	0.0256 (8)	0.0466 (9)	0.0316 (7)	0.0043 (6)	−0.0001 (6)	−0.0049 (7)
O1	0.0307 (7)	0.0477 (8)	0.0437 (7)	0.0115 (6)	−0.0002 (5)	−0.0040 (6)
O2	0.0367 (7)	0.0580 (8)	0.0302 (6)	−0.0009 (6)	−0.0039 (5)	−0.0001 (6)
O3	0.0254 (7)	0.0589 (9)	0.0530 (8)	−0.0023 (6)	0.0004 (6)	−0.0042 (7)
O4	0.0382 (8)	0.0584 (9)	0.0541 (8)	0.0136 (7)	−0.0054 (6)	0.0154 (7)
Cl1	0.0433 (3)	0.0341 (2)	0.0463 (3)	0.00160 (18)	0.0065 (2)	0.01473 (18)
C8	0.0429 (11)	0.0369 (9)	0.0287 (8)	0.0107 (8)	0.0059 (7)	0.0010 (7)
C9	0.0295 (9)	0.0400 (10)	0.0323 (8)	0.0069 (7)	0.0027 (7)	0.0002 (7)
C10	0.0306 (9)	0.0360 (9)	0.0214 (7)	0.0035 (7)	0.0037 (6)	−0.0002 (6)
C11	0.0282 (9)	0.0381 (9)	0.0262 (8)	0.0056 (7)	0.0033 (6)	0.0018 (7)

C12	0.0316 (9)	0.0472 (10)	0.0266 (8)	−0.0011 (7)	0.0030 (7)	0.0004 (7)
N2	0.0440 (9)	0.0359 (8)	0.0275 (7)	−0.0008 (7)	0.0060 (6)	0.0002 (6)
N3	0.0289 (8)	0.0361 (8)	0.0435 (9)	0.0021 (7)	−0.0018 (7)	−0.0013 (7)
O1W	0.249 (4)	0.0447 (10)	0.0407 (10)	0.0464 (14)	0.0425 (14)	0.0092 (9)

Geometric parameters (Å, º)

C1—C2	1.395 (2)	C8—N2	1.347 (2)
C1—C6	1.398 (2)	C8—C9	1.353 (3)
C1—C7	1.515 (2)	C8—H8	0.95
C2—C3	1.381 (2)	C9—C10	1.418 (2)
C2—Cl1	1.7369 (16)	C9—H9	0.95
C3—C4	1.381 (2)	C10—N3	1.334 (2)
C3—H3	0.95	C10—C11	1.407 (2)
C4—C5	1.376 (2)	C11—C12	1.358 (2)
C4—N1	1.471 (2)	C11—H11	0.95
C5—C6	1.383 (2)	C12—N2	1.345 (2)
C5—H5	0.95	C12—H12	0.95
C6—H6	0.95	N2—H2	0.93 (3)
C7—O2	1.248 (2)	N3—H3A	0.94 (2)
C7—O1	1.248 (2)	N3—H3B	0.84 (2)
N1—O3	1.219 (2)	O1W—H1W	0.75 (3)
N1—O4	1.230 (2)	O1W—H2W	0.78 (4)
C2—C1—C6	118.13 (15)	O4—N1—C4	117.71 (15)
C2—C1—C7	122.05 (14)	N2—C8—C9	121.43 (16)
C6—C1—C7	119.83 (14)	N2—C8—H8	119.3
C3—C2—C1	121.91 (15)	C9—C8—H8	119.3
C3—C2—Cl1	118.28 (12)	C8—C9—C10	119.60 (17)
C1—C2—Cl1	119.80 (12)	C8—C9—H9	120.2
C4—C3—C2	117.63 (15)	C10—C9—H9	120.2
C4—C3—H3	121.2	N3—C10—C11	121.74 (16)
C2—C3—H3	121.2	N3—C10—C9	120.92 (16)
C5—C4—C3	122.84 (15)	C11—C10—C9	117.33 (16)
C5—C4—N1	118.88 (15)	C12—C11—C10	119.83 (16)
C3—C4—N1	118.27 (15)	C12—C11—H11	120.1
C4—C5—C6	118.46 (15)	C10—C11—H11	120.1
C4—C5—H5	120.8	N2—C12—C11	121.31 (17)
C6—C5—H5	120.8	N2—C12—H12	119.3
C5—C6—C1	121.02 (16)	C11—C12—H12	119.3
C5—C6—H6	119.5	C12—N2—C8	120.46 (16)
C1—C6—H6	119.5	C12—N2—H2	118.9 (15)
O2—C7—O1	126.79 (16)	C8—N2—H2	120.3 (15)
O2—C7—C1	116.89 (15)	C10—N3—H3A	118.3 (13)
O1—C7—C1	116.28 (14)	C10—N3—H3B	116.1 (15)
O3—N1—O4	124.01 (15)	H3A—N3—H3B	126 (2)
O3—N1—C4	118.28 (15)	H1W—O1W—H2W	117 (3)

C6—C1—C2—C3	0.4 (2)	C2—C1—C7—O1	99.31 (18)
C7—C1—C2—C3	−179.64 (14)	C6—C1—C7—O1	−80.7 (2)
C6—C1—C2—Cl1	179.99 (12)	C5—C4—N1—O3	−179.69 (15)
C7—C1—C2—Cl1	0.0 (2)	C3—C4—N1—O3	−0.8 (2)
C1—C2—C3—C4	−0.6 (2)	C5—C4—N1—O4	−0.2 (2)
Cl1—C2—C3—C4	179.75 (12)	C3—C4—N1—O4	178.68 (15)
C2—C3—C4—C5	0.1 (2)	N2—C8—C9—C10	0.8 (3)
C2—C3—C4—N1	−178.79 (14)	C8—C9—C10—N3	178.61 (16)
C3—C4—C5—C6	0.8 (3)	C8—C9—C10—C11	−1.9 (2)
N1—C4—C5—C6	179.59 (14)	N3—C10—C11—C12	−178.78 (16)
C4—C5—C6—C1	−1.0 (3)	C9—C10—C11—C12	1.8 (2)
C2—C1—C6—C5	0.5 (2)	C10—C11—C12—N2	−0.5 (2)
C7—C1—C6—C5	−179.52 (15)	C11—C12—N2—C8	−0.8 (2)
C2—C1—C7—O2	−82.6 (2)	C9—C8—N2—C12	0.6 (2)
C6—C1—C7—O2	97.40 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1*W*^{i}	0.93 (3)	1.72 (3)	2.641 (2)	170 (2)
N3—H3*A*···O1	0.94 (2)	1.99 (2)	2.926 (2)	171.1 (19)
N3—H3*B*···O2^{ii}	0.84 (2)	2.16 (3)	2.982 (2)	165 (2)
O1*W*—H1*W*···O1^{iii}	0.75 (3)	1.96 (3)	2.698 (2)	166 (3)
O1*W*—H2*W*···O2	0.78 (4)	1.99 (4)	2.729 (2)	158 (3)

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