Crystal structures of three halide salts of L-asparagine: an isostructural series

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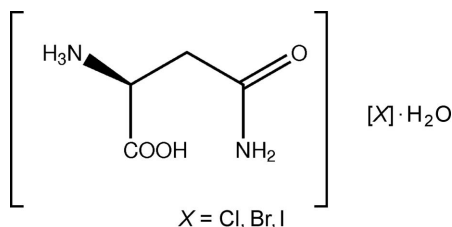
The structures of three monohydrated halide salt forms of L-asparagine are presented, $viz.$ L-asparaginium chloride monohydrate, $C_4H_9N_2O_3^+ \cdot Cl^- \cdot H_2O$, (I), L-asparaginium bromide monohydrate, $C_4H_9N_2O_3^+ \cdot Br^- \cdot H_2O$, (II), and L-asparaginium iodide monohydrate, $C_4H_9N_2O_3^+ \cdot I^- \cdot H_2O$, (III). These form an isomorphous and isostructural series. The C—C—C—C backbone of the amino acid adopts a $gauche$ conformation in each case [torsion angles for (I), (II) and (III) = −55.4 (2), −55.6 (5) and −58.3 (7)°, respectively]. Each cation features an intramolecular N—H···O hydrogen bond, which closes an S(6) ring. The extended structures feature chains of cations that propagate parallel to the b-axis direction. These are formed by carboxylic acid/amide complimentary O—H···O + N—H···O hydrogen bonds, which generate $R_2^2(8)$ loops. These chains are linked by further hydrogen bonds mediated by the halide ions and water molecules to give a layered structure with cation and anion layers parallel to the ab plane. Compound (III) was refined as an inversion twin.

1. Chemical context

Changing the salt form of an organic material is a well known way of altering the material's physical properties whilst retaining many of the chemical properties inherent to the organic fragment. Selection of the salt form with the most suitable properties is thus an important consideration in the development of pharmaceutical materials and indeed of other fine chemicals (Stahl & Wermuth, 2008; Bastin *et al.*, 2000; Kennedy *et al.*, 2012). Often, the main property of interest is solubility, but salt selection may also be used to alter properties such as crystal morphology, hygroscopicity or stability, as well as mechanical properties such as hardness and strength (Stahl & Wermuth, 2008; Sun & Grant, 2001; Hao & Iqbal, 1997; de Moraes *et al.*, 2017). In short, any bulk property that depends in some way on the packing or on the intermolecular forces within the crystalline array structure may be altered by changing the salt-forming counter-ion. Despite the common usage of salt selection strategies, our understanding of what effect on properties any particular change of counter-ion will have is extremely limited. This means, for example, that it is not currently possible to predict which salt form of an active pharmaceutical ingredient (API) will be the most soluble or have the best compaction properties. In this area, isostructural series of structures are especially interesting as they allow changes in properties to be related to changes in intermolecular interaction strength or type without the complication of changes to the overall gross structure (Galcera & Molins, 2009; Allan *et al.*, 2018). Here we present the structures of three isostructural halide salts of L-asparagine, namely

the monohydrates [HAsp][Cl]·H_2O, (I), [HAsp][Br]·H_2O, (II) and [HAsp][I]·H_2O, (III), (HAsp = $C_4H_9N_2O_3$ cation). L-asparagine is a non-essential amino acid, the bioavailability of which is associated with altered rates of breast cancer progression (Knott *et al.*, 2018).

H_3N ... O ... [X]·H_2O ... COOH ... NH_2

X = Cl, Br, I

2. Structural commentary

The crystals isolated from all three reactions of L-asparagine with HX (X = Cl, Br, I) solutions were found to be hydrated compounds with the formula [HAsp][X]·H_2O with protonation occurring at N1 as well as at the carboxylic acid. The starting material used was labelled L-asparagine and in all cases the refined Flack parameter confirmed that, as expected, this is S-asparagine.

Crystals (I), (II) and (III) were found to adopt the same space group and to have similar unit-cell dimensions. They thus represent an isostructural series, with the unit-cell dimensions increasing as expected in line with increasing halide ion size. The HAsp cations are found to have near identical geometries. All equivalent bond lengths are statistically similar and all cations adopt the same general conformation with both C=O units *syn* with respect to the NH_3 group, see Figs. 1–3. There are some small differences within this general conformation. The largest of these differences occurs between the iodide salt and the others, as indicated by the torsion angles involving the NH_3 group [N1—C2—C1—O1 (acid C=O) = 24.6 (2), 20.2 (5) and 12.5 (8) and N1—C2—C4—O3 (amide) 27.1 (2), 27.73 (5) and 33.38 (8)°, for Cl, Br and I respectively].

Figure 2
View of the contents of the asymmetric unit of (II). Non-H atoms are drawn as 50% probability ellipsoids and H atoms as spheres of arbitrary size.

3. Supramolecular features

Isostructurality is also indicated by examination of the hydrogen bonding, Tables 1–3 and Fig. 4. The three compounds all make the same number and type of hydrogen bonds, with the main difference being the increasing $D\cdots A$ distances caused by the different anion sizes. Where $A = X$ there is a 7.4 to 11.5% increase in $D\cdots A$ distance from Cl to I, whereas where $A = O$ there is a smaller 0.6 to 4.0% increase. The only exception is the sole intramolecular interaction. The $D\cdots A$ distance of this NH_3 to amide contact decreases by about 1.5% from Cl to I.

The only HAsp to HAsp hydrogen bonds form the classic carboxylic acid to amide O—H$\cdots$O + N—H$\cdots$O heterodimer motif [$R(8)^2_2$]. With two such contacts per cation, this motif generates a one-dimensional hydrogen-bonded chain running parallel to the b-axis direction, see Fig. 5. Additionally, each
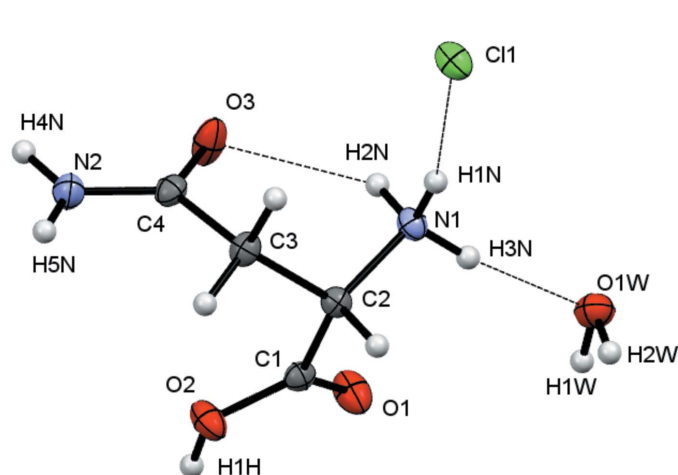

Figure 1
View of the contents of the asymmetric unit of (I). Non-H atoms are drawn as 50% probability ellipsoids and H atoms as spheres of arbitrary size.

Figure 3
View of the contents of the asymmetric unit of (III). Non-H atoms are drawn as 50% probability ellipsoids and H atoms as spheres of arbitrary size.

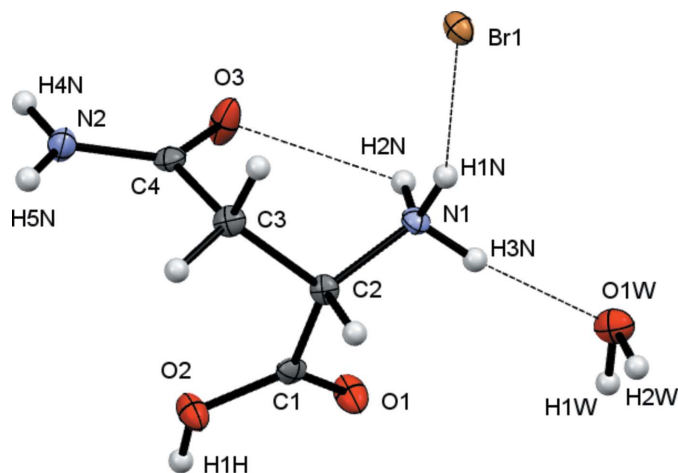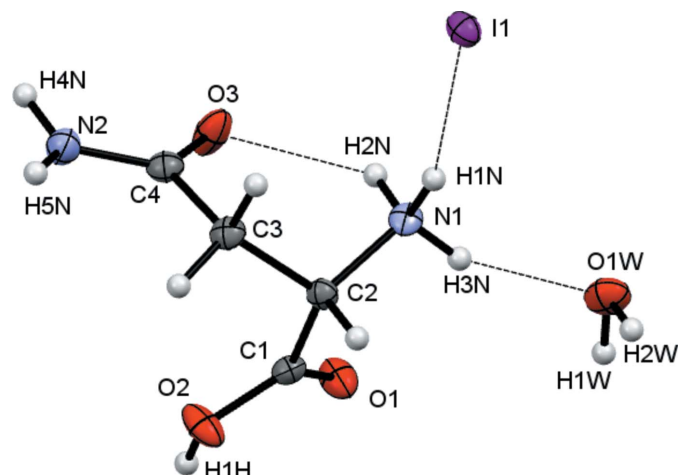**Table 1**
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H1$H\cdots$O3^i	0.88 (1)	1.66 (2)	2.533 (2)	172 (4)
N1—H1$N\cdots$Cl1	0.91 (1)	2.27 (1)	3.1663 (17)	166 (2)
N1—H2$N\cdots$Cl1^{ii}	0.89 (1)	2.56 (2)	3.2909 (17)	140 (2)
N1—H2$N\cdots$O3	0.89 (1)	2.19 (2)	2.809 (2)	126 (2)
N1—H3$N\cdots$O1W	0.90 (1)	1.97 (1)	2.867 (2)	172 (2)
N2—H4$N\cdots$Cl1^{iii}	0.90 (1)	2.89 (2)	3.4056 (17)	118 (2)
N2—H4$N\cdots$O1^{iv}	0.90 (1)	2.21 (2)	3.051 (2)	156 (2)
N2—H5$N\cdots$O1W^v	0.88 (1)	2.08 (1)	2.949 (2)	167 (2)
O1W—H1$W\cdots$Cl1^{vi}	0.87 (1)	2.41 (1)	3.2650 (18)	169 (2)
O1W—H2$W\cdots$Cl1^{vii}	0.87 (1)	2.40 (2)	3.2184 (17)	157 (2)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H1$H\cdots$O3^i	0.88 (1)	1.68 (2)	2.543 (4)	167 (6)
N1—H1$N\cdots$Br1	0.90 (1)	2.46 (2)	3.314 (5)	159 (4)
N1—H2$N\cdots$Br1^{ii}	0.89 (1)	2.59 (3)	3.408 (5)	153 (4)
N1—H2$N\cdots$O3	0.89 (1)	2.30 (5)	2.787 (6)	114 (4)
N1—H3$N\cdots$O1W	0.90 (1)	1.99 (2)	2.886 (4)	173 (5)
N2—H4$N\cdots$Br1^{iii}	0.90 (1)	2.95 (4)	3.479 (4)	119 (4)
N2—H4$N\cdots$O1^{iv}	0.90 (1)	2.26 (3)	3.081 (5)	152 (4)
N2—H5$N\cdots$O1W^v	0.90 (1)	2.07 (2)	2.959 (6)	170 (5)
O1W—H1$W\cdots$Br1^{vi}	0.88 (1)	2.51 (2)	3.362 (4)	167 (5)
O1W—H2$W\cdots$Br1^{vii}	0.88 (1)	2.61 (4)	3.323 (4)	138 (5)

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

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H1$H\cdots$O3^i	0.88 (1)	1.71 (3)	2.549 (6)	160 (9)
N1—H1$N\cdots$I1	0.91	2.65	3.528 (7)	164
N1—H2$N\cdots$I1^{ii}	0.91	2.89	3.591 (8)	135
N1—H2$N\cdots$O3	0.91	2.11	2.766 (8)	129
N1—H3$N\cdots$O1W	0.91	2.03	2.905 (6)	160
N2—H4$N\cdots$I1^{iii}	0.90 (1)	3.07 (6)	3.659 (5)	125 (5)
N2—H4$N\cdots$O1^{iv}	0.90 (1)	2.37 (4)	3.171 (7)	149 (6)
N2—H5$N\cdots$O1W^v	0.90 (1)	2.12 (3)	2.983 (9)	160 (7)
O1W—H1$W\cdots$I1^{vi}	0.88 (1)	2.68 (2)	3.526 (8)	164 (5)
O1W—H2$W\cdots$I1^{vii}	0.88 (1)	2.76 (4)	3.504 (7)	143 (6)

Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + 1$; (ii) $x + 1, y, z$; (iii) $x, y, z - 1$; (iv) $-x + 2, y + \frac{1}{2}, -z + 1$; (v) $x - 1, y, z - 1$; (vi) $-x + 2, y - \frac{1}{2}, -z + 2$; (vii) $-x + 1, y - \frac{1}{2}, -z + 2$.
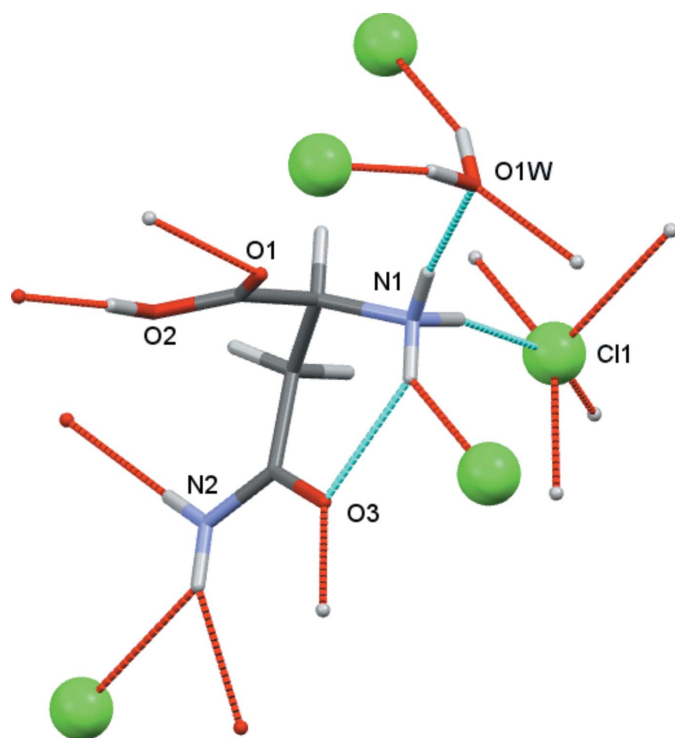
halide ion accepts five unique hydrogen bonds, two bonds from water molecules, two from NH$_3$ groups and one from NH$_2$. The water molecules donate two hydrogen bonds to the halide ions and accept two from the NH$_3$ and NH$_2$ groups. The water molecules thus form fourfold nodes, as is typical for
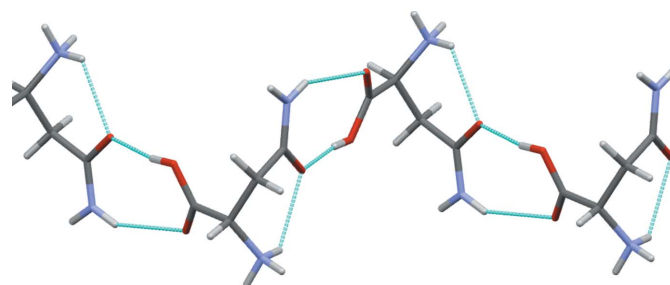

Figure 5
Chain of cations in (II) propagating parallel to the b-axis direction *via* O—H$\cdots$O and O—H$\cdots$N carboxylic acid to amide hydrogen bonds.
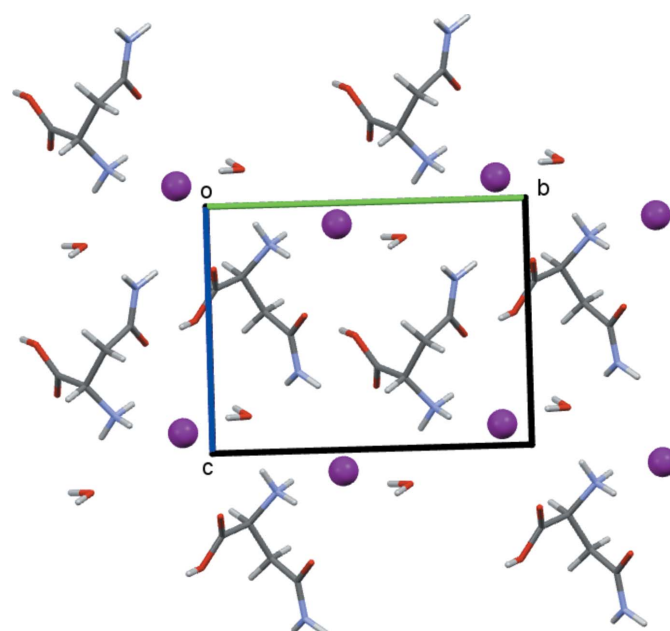

Figure 4
View of all the unique hydrogen-bonding contacts made by the contents of the asymmetric unit of (I).

Figure 6
Packing diagram of (III) as viewed down the a-axis direction.

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_4H_9N_2O_3^+ \cdot Cl^- \cdot H_2O$	$C_4H_9N_2O_3^- \cdot Br^+ \cdot H_2O$	$C_4H_9N_2O_3^+ \cdot I^- \cdot H_2O$
M_r	186.60	231.06	278.05
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Monoclinic, $P2_1$
Temperature (K)	123	123	123
a, b, c (Å)	5.0922 (1), 10.1450 (2), 8.1950 (2)	5.2167 (2), 10.2784 (5), 8.3063 (4)	5.3668 (5), 10.6744 (8), 8.4532 (6)
β (°)	103.834 (2)	103.606 (5)	102.772 (8)
V (Å³)	411.08 (2)	432.88 (4)	472.28 (7)
Z	2	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm⁻¹)	0.44	4.72	3.37
Crystal size (mm)	$0.45 \times 0.30 \times 0.25$	$0.5 \times 0.3 \times 0.12$	$0.6 \times 0.35 \times 0.15$
Data collection			
Diffractometer	Oxford Diffraction Xcalibur E	Oxford Diffraction Xcalibur E	Oxford Diffraction Xcalibur E
Absorption correction	Multi-scan [*CrysAlis PRO* (Agilent, 2014), based on expressions derived by Clark & Reid (1995)]	Analytical [*CrysAlis PRO* (Agilent, 2014), based on expressions derived by Clark & Reid (1995)]	Analytical [*CrysAlis PRO* (Agilent, 2014), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.900, 1.000	0.205, 0.487	0.286, 0.612
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4053, 2079, 2032	4320, 2232, 2118	5854, 2458, 2288
R_{int}	0.013	0.032	0.039
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.698	0.700	0.702
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.058, 1.07	0.028, 0.062, 1.03	0.029, 0.058, 1.02
No. of reflections	2079	2232	2458
No. of parameters	128	128	117
No. of restraints	9	9	7
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	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.26, −0.20	0.60, −0.38	0.87, −0.65
Absolute structure	Flack x determined using 897 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)	Flack x determined using 908 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)	Refined as an inversion twin
Absolute structure parameter	−0.02 (2)	−0.022 (11)	−0.07 (4)

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1994), *SHELXL2014* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2008).

organic hydrates (Gillon *et al.*, 2003; Briggs *et al.*, 2012). These interactions combine to give the structure shown in Fig. 6 with alternating layers of organic cations and halide anions lying parallel to the *ab* plane.

4. Database survey

The only other known structure of a simple salt of *S*-asparagine is that of the nitrate (Aarthy *et al.*, 2005). Here both the cations in a $Z' = 2$ structure adopt different conformations from that found for the halides: compare N—C—C—O(acid C=O) of −176.9 (6) and 173.2 (5)° and N—C—C—O(amide) of −123.2 (7) and 77.0 (4)° with the equivalent values given above. The structures of two simple salts of racemic asparagine have also been reported. These are the nitrate and the perchlorate forms (Moussa Slimane *et al.*, 2009; Guenifa *et al.*, 2009). All these literature forms are anhydrous, but despite this difference and further differences in anion type and cation geometry, all form the same $R(8)_2^2$-based, one-dimensional hydrogen-bonded chain motif seen in the halide salts (I), (II) and (III).

5. Synthesis and crystallization

Salt forms of L-asparagine were prepared by dissolving 29 mmol of the amino acid in 90 ml of distilled water. The solution was stirred and heated slightly until complete dissolution had occurred. The solution was then equally divided between three vials. To each vial was added 1 ml of concentrated acid, either hydrochloric acid, hydrobromic acid or hydroiodic acid. The first crystals appeared after 24 h of sitting at room temperature. Crystals suitable for analyses [colourless prisms for (I), colourless tablets for (II) and colourless rods for (III)] were obtained directly from the mother liquors and were removed from these solutions just prior to data collection.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Structure solution for (III) was by substitution from the Br equivalent. All H atoms bound to C were placed in calculated positions and refined in riding modes. C—H distances were 0.99 and 1.00 Å for CH₂ and CH

groups respectively, with $U(H)_{iso} = 1.2U_{eq}(C)$. With the exception noted below, all other H atoms were observed and positioned as found. For (I) these were refined isotropically, but for (II) restraints were required for the NH_3 and OH_2 atoms. For (III) all H atoms required restraints to be applied. N—H distances were restrained to 0.90 (1) Å and O—H distances to 0.88 (1) Å. $U(H)_{iso} = 1.2U_{eq}$ of the parent atom. The exception was the NH_3 group of (III). The best model involved treating this as a rigid tetrahedral group and allowing only rotation around the C—N bond. For this group, $U_{iso}(H) = 1.5U_{eq}(N)$. Compound (III) was refined as an inversion twin.

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Computing details

For all structures, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I), (II); by substitution from Br equivalent for (III). For all structures, program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

***L*-Asparaginium chloride monohydrate (I)**

Crystal data

$C_4H_9N_2O_3{}^+{\cdot}Cl^-{\cdot}H_2O$	$F(000) = 196$
$M_r = 186.60$	$D_x = 1.508$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.0922$ (1) Å	Cell parameters from 3444 reflections
$b = 10.1450$ (2) Å	$\theta = 3.3–29.7°$
$c = 8.1950$ (2) Å	$\mu = 0.44$ mm^{-1}
$\beta = 103.834$ (2)°	$T = 123$ K
$V = 411.08$ (2) Å^3	Prism, colourless
$Z = 2$	$0.45 \times 0.30 \times 0.25$ mm

Data collection

Oxford Diffraction Xcalibur E diffractometer	4053 measured reflections
Radiation source: sealed tube	2079 independent reflections
ω scans	2032 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan [CrysAlis PRO (Agilent, 2014), based on expressions derived by Clark & Reid (1995)]	$R_{int} = 0.013$
	$\theta_{max} = 29.8°$, $\theta_{min} = 3.3°$
	$h = -7{\rightarrow}7$
	$k = -14{\rightarrow}13$
$T_{min} = 0.900$, $T_{max} = 1.000$	$l = -10{\rightarrow}10$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.0289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2079 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
128 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
9 restraints	Extinction correction: SHELXL-2014/7 (Sheldrick 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	
Hydrogen site location: mixed	Extinction coefficient: 0.029 (8)

Absolute structure: Flack x determined using
897 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: −0.02 (2)

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	0.36571 (8)	0.90075 (4)	0.92401 (5)	0.02062 (13)
O1	1.1145 (3)	0.51257 (16)	0.77258 (18)	0.0258 (3)
O2	0.8130 (3)	0.48931 (15)	0.52673 (18)	0.0237 (3)
O3	0.8617 (3)	0.83494 (16)	0.56812 (17)	0.0269 (3)
O1W	1.1611 (3)	0.58702 (15)	1.1607 (2)	0.0242 (3)
H1W	1.275 (4)	0.528 (2)	1.142 (3)	0.029*
H2W	1.034 (4)	0.532 (2)	1.170 (3)	0.029*
N1	0.8288 (3)	0.71004 (16)	0.8685 (2)	0.0162 (3)
H1N	0.699 (4)	0.758 (2)	0.902 (3)	0.019*
H2N	0.936 (4)	0.764 (2)	0.827 (3)	0.019*
H3N	0.927 (4)	0.664 (2)	0.957 (2)	0.019*
N2	0.5625 (4)	0.78473 (17)	0.3247 (2)	0.0218 (4)
C1	0.8969 (4)	0.53507 (18)	0.6792 (2)	0.0153 (3)
C2	0.6864 (4)	0.61977 (17)	0.7318 (2)	0.0140 (3)
H1	0.5703	0.5597	0.7813	0.017*
C3	0.5009 (4)	0.69279 (18)	0.5859 (2)	0.0162 (3)
H2	0.3900	0.6278	0.5091	0.019*
H3	0.3765	0.7499	0.6304	0.019*
C4	0.6548 (4)	0.77587 (19)	0.4888 (2)	0.0170 (4)
H1H	0.936 (6)	0.437 (3)	0.503 (5)	0.067 (11)*
H4N	0.643 (4)	0.8399 (19)	0.266 (3)	0.019 (6)*
H5N	0.423 (4)	0.736 (2)	0.273 (3)	0.023 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01624 (19)	0.0241 (2)	0.0209 (2)	0.00077 (17)	0.00325 (14)	−0.00539 (18)
O1	0.0182 (7)	0.0346 (8)	0.0224 (7)	0.0096 (6)	0.0008 (5)	−0.0059 (6)
O2	0.0211 (7)	0.0281 (8)	0.0204 (7)	0.0067 (6)	0.0020 (5)	−0.0079 (6)
O3	0.0222 (7)	0.0359 (8)	0.0199 (7)	−0.0128 (6)	0.0000 (6)	0.0078 (6)
O1W	0.0252 (8)	0.0200 (7)	0.0270 (8)	−0.0019 (6)	0.0051 (6)	−0.0003 (6)
N1	0.0150 (8)	0.0182 (8)	0.0156 (8)	0.0008 (6)	0.0040 (6)	−0.0019 (6)
N2	0.0265 (9)	0.0217 (8)	0.0163 (7)	−0.0029 (7)	0.0034 (7)	0.0011 (6)
C1	0.0149 (8)	0.0149 (8)	0.0168 (8)	−0.0014 (6)	0.0052 (6)	0.0014 (6)
C2	0.0123 (8)	0.0149 (8)	0.0152 (8)	−0.0006 (6)	0.0039 (6)	−0.0007 (6)

C3	0.0129 (8)	0.0186 (8)	0.0166 (8)	0.0004 (7)	0.0026 (6)	0.0023 (7)
C4	0.0168 (8)	0.0163 (8)	0.0183 (8)	0.0023 (6)	0.0046 (7)	0.0023 (6)

Geometric parameters (Å, º)

O1—C1	1.209 (2)	N2—C4	1.317 (2)
O2—C1	1.305 (2)	N2—H4N	0.897 (12)
O2—H1H	0.876 (13)	N2—H5N	0.882 (13)
O3—C4	1.251 (2)	C1—C2	1.515 (2)
O1W—H1W	0.869 (13)	C2—C3	1.527 (2)
O1W—H2W	0.868 (13)	C2—H1	1.0000
N1—C2	1.493 (2)	C3—C4	1.502 (3)
N1—H1N	0.913 (13)	C3—H2	0.9900
N1—H2N	0.891 (13)	C3—H3	0.9900
N1—H3N	0.901 (12)		
C1—O2—H1H	110 (3)	N1—C2—C3	112.85 (15)
H1W—O1W—H2W	97 (3)	C1—C2—C3	113.57 (15)
C2—N1—H1N	107.3 (15)	N1—C2—H1	107.3
C2—N1—H2N	108.8 (17)	C1—C2—H1	107.3
H1N—N1—H2N	110 (2)	C3—C2—H1	107.3
C2—N1—H3N	111.2 (16)	C4—C3—C2	112.56 (15)
H1N—N1—H3N	109 (2)	C4—C3—H2	109.1
H2N—N1—H3N	110 (2)	C2—C3—H2	109.1
C4—N2—H4N	119.5 (15)	C4—C3—H3	109.1
C4—N2—H5N	119.9 (17)	C2—C3—H3	109.1
H4N—N2—H5N	121 (2)	H2—C3—H3	107.8
O1—C1—O2	125.44 (17)	O3—C4—N2	123.25 (18)
O1—C1—C2	122.06 (16)	O3—C4—C3	118.34 (16)
O2—C1—C2	112.48 (15)	N2—C4—C3	118.40 (17)
N1—C2—C1	108.17 (14)		
O1—C1—C2—N1	24.6 (2)	N1—C2—C3—C4	68.1 (2)
O2—C1—C2—N1	−156.61 (16)	C1—C2—C3—C4	−55.4 (2)
O1—C1—C2—C3	150.72 (17)	C2—C3—C4—O3	−37.7 (2)
O2—C1—C2—C3	−30.5 (2)	C2—C3—C4—N2	143.49 (18)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1H···O3[i]	0.88 (1)	1.66 (2)	2.533 (2)	172 (4)
N1—H1N···Cl1	0.91 (1)	2.27 (1)	3.1663 (17)	166 (2)
N1—H2N···Cl1[ii]	0.89 (1)	2.56 (2)	3.2909 (17)	140 (2)
N1—H2N···O3	0.89 (1)	2.19 (2)	2.809 (2)	126 (2)
N1—H3N···O1W	0.90 (1)	1.97 (1)	2.867 (2)	172 (2)
N2—H4N···Cl1[iii]	0.90 (1)	2.89 (2)	3.4056 (17)	118 (2)
N2—H4N···O1[iv]	0.90 (1)	2.21 (2)	3.051 (2)	156 (2)
N2—H5N···O1W[v]	0.88 (1)	2.08 (1)	2.949 (2)	167 (2)

O1W—H1W···Cl1^{vi}	0.87 (1)	2.41 (1)	3.2650 (18)	169 (2)
O1W—H2W···Cl1^{vii}	0.87 (1)	2.40 (2)	3.2184 (17)	157 (2)

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

L-Asparaginium bromide monohydrate (II)

Crystal data

$C_4H_9N_2O_3^-·Br^+·H_2O$
$M_r = 231.06$
Monoclinic, $P2_1$
$a = 5.2167$ (2) Å
$b = 10.2784$ (5) Å
$c = 8.3063$ (4) Å
$\beta = 103.606$ (5)°
$V = 432.88$ (4) Å^3
$Z = 2$

$F(000) = 232$
$D_x = 1.773$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3145 reflections
$\theta = 3.2$–29.8°
$\mu = 4.72$ mm^{-1}
$T = 123$ K
Tablet, colourless
0.5 × 0.3 × 0.12 mm

Data collection

Oxford Diffraction Xcalibur E
   diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: analytical
   [CrysAlis PRO (Agilent, 2014), based on
   expressions derived by Clark & Reid (1995)]
$T_{min} = 0.205$, $T_{max} = 0.487$

4320 measured reflections
2232 independent reflections
2118 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 29.8°$, $\theta_{min} = 3.2°$
$h = -7 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.062$
$S = 1.03$
2232 reflections
128 parameters
9 restraints
Primary atom site location: structure-invariant
   direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent
   and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: SHELXL2014
   (Sheldrick, 2015),
   Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.019 (3)
Absolute structure: Flack x determined using
   908 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons et al.,
   2013)
Absolute structure parameter: −0.022 (11)

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}
Br1	0.36490 (6)	0.90306 (8)	0.92345 (4)	0.01479 (13)

O1	1.1176 (6)	0.5163 (3)	0.7609 (4)	0.0196 (7)
O2	0.8106 (6)	0.4779 (3)	0.5270 (4)	0.0187 (7)
O3	0.8665 (6)	0.8262 (3)	0.5653 (4)	0.0226 (7)
O1W	1.1602 (8)	0.5964 (4)	1.1565 (6)	0.0196 (9)
H1W	1.274 (8)	0.536 (4)	1.147 (7)	0.024*
H2W	1.059 (10)	0.541 (5)	1.193 (7)	0.024*
N1	0.8287 (9)	0.7034 (5)	0.8580 (6)	0.0124 (9)
H1N	0.716 (8)	0.749 (4)	0.903 (6)	0.015*
H2N	0.951 (8)	0.757 (4)	0.836 (6)	0.015*
H3N	0.932 (8)	0.663 (5)	0.947 (4)	0.015*
N2	0.5699 (7)	0.7822 (4)	0.3244 (4)	0.0169 (8)
C1	0.8998 (8)	0.5314 (4)	0.6731 (5)	0.0124 (8)
C2	0.6900 (8)	0.6143 (4)	0.7242 (5)	0.0109 (8)
H1	0.5765	0.5549	0.7729	0.013*
C3	0.5124 (8)	0.6858 (4)	0.5811 (5)	0.0130 (8)
H2	0.4071	0.6215	0.5044	0.016*
H3	0.3884	0.7411	0.6243	0.016*
C4	0.6627 (8)	0.7697 (4)	0.4866 (5)	0.0132 (8)
H1H	0.938 (9)	0.428 (5)	0.509 (8)	0.046 (18)*
H4N	0.645 (9)	0.837 (4)	0.265 (5)	0.016 (12)*
H5N	0.431 (7)	0.733 (4)	0.276 (6)	0.016 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01205 (18)	0.01658 (19)	0.01513 (18)	0.0006 (2)	0.00197 (12)	−0.0034 (2)
O1	0.0120 (15)	0.0263 (18)	0.0185 (16)	0.0072 (13)	−0.0002 (13)	−0.0061 (13)
O2	0.0148 (14)	0.0238 (17)	0.0159 (15)	0.0046 (13)	0.0003 (12)	−0.0062 (13)
O3	0.0176 (16)	0.0309 (19)	0.0159 (15)	−0.0127 (13)	−0.0031 (13)	0.0076 (14)
O1W	0.015 (2)	0.018 (2)	0.025 (2)	−0.0018 (17)	0.0022 (16)	0.0001 (17)
N1	0.013 (2)	0.012 (2)	0.012 (2)	0.0026 (18)	0.0035 (17)	−0.0018 (17)
N2	0.0205 (19)	0.0169 (18)	0.0123 (17)	−0.0031 (16)	0.0013 (15)	0.0014 (14)
C1	0.014 (2)	0.0102 (18)	0.0142 (19)	−0.0021 (15)	0.0056 (16)	0.0019 (15)
C2	0.0072 (18)	0.0129 (19)	0.0124 (18)	−0.0021 (15)	0.0020 (15)	−0.0005 (15)
C3	0.0092 (18)	0.014 (2)	0.016 (2)	−0.0008 (16)	0.0018 (16)	0.0003 (16)
C4	0.0135 (19)	0.0099 (19)	0.0158 (19)	0.0025 (16)	0.0024 (16)	0.0017 (15)

Geometric parameters (Å, º)

O1—C1	1.207 (5)	N2—C4	1.326 (5)
O2—C1	1.314 (5)	N2—H4N	0.898 (14)
O2—H1H	0.879 (14)	N2—H5N	0.897 (14)
O3—C4	1.252 (5)	C1—C2	1.524 (6)
O1W—H1W	0.875 (14)	C2—C3	1.515 (6)
O1W—H2W	0.879 (14)	C2—H1	1.0000
N1—C2	1.490 (6)	C3—C4	1.504 (6)
N1—H1N	0.900 (14)	C3—H2	0.9900
N1—H2N	0.894 (14)	C3—H3	0.9900

N1—H3N	0.904 (14)		

C1—O2—H1H	106 (4)	N1—C2—C1	107.3 (3)
H1W—O1W—H2W	93 (5)	C3—C2—C1	113.5 (3)
C2—N1—H1N	112 (3)	N1—C2—H1	107.7
C2—N1—H2N	118 (3)	C3—C2—H1	107.7
H1N—N1—H2N	109 (5)	C1—C2—H1	107.7
C2—N1—H3N	115 (4)	C4—C3—C2	113.0 (3)
H1N—N1—H3N	102 (4)	C4—C3—H2	109.0
H2N—N1—H3N	98 (5)	C2—C3—H2	109.0
C4—N2—H4N	121 (3)	C4—C3—H3	109.0
C4—N2—H5N	118 (3)	C2—C3—H3	109.0
H4N—N2—H5N	121 (5)	H2—C3—H3	107.8
O1—C1—O2	125.7 (4)	O3—C4—N2	123.2 (4)
O1—C1—C2	122.6 (4)	O3—C4—C3	118.4 (4)
O2—C1—C2	111.7 (4)	N2—C4—C3	118.4 (4)
N1—C2—C3	112.8 (3)		

O1—C1—C2—N1	20.2 (5)	N1—C2—C3—C4	66.7 (5)
O2—C1—C2—N1	−161.4 (4)	C1—C2—C3—C4	−55.6 (5)
O1—C1—C2—C3	145.4 (4)	C2—C3—C4—O3	−35.7 (5)
O2—C1—C2—C3	−36.1 (5)	C2—C3—C4—N2	145.6 (4)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H1H⋯O3[i]	0.88 (1)	1.68 (2)	2.543 (4)	167 (6)
N1—H1N⋯Br1	0.90 (1)	2.46 (2)	3.314 (5)	159 (4)
N1—H2N⋯Br1[ii]	0.89 (1)	2.59 (3)	3.408 (5)	153 (4)
N1—H2N⋯O3	0.89 (1)	2.30 (5)	2.787 (6)	114 (4)
N1—H3N⋯O1W	0.90 (1)	1.99 (2)	2.886 (4)	173 (5)
N2—H4N⋯Br1[iii]	0.90 (1)	2.95 (4)	3.479 (4)	119 (4)
N2—H4N⋯O1[iv]	0.90 (1)	2.26 (3)	3.081 (5)	152 (4)
N2—H5N⋯O1W[v]	0.90 (1)	2.07 (2)	2.959 (6)	170 (5)
O1W—H1W⋯Br1[vi]	0.88 (1)	2.51 (2)	3.362 (4)	167 (5)
O1W—H2W⋯Br1[vii]	0.88 (1)	2.61 (4)	3.323 (4)	138 (5)

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

L-Asparaginium iodide monohydrate (III)

Crystal data

$C_4H_9N_2O_3{}^+·I^-·H_2O$	$V = 472.28 (7)$ Å^3
$M_r = 278.05$	$Z = 2$
Monoclinic, $P2_1$	$F(000) = 268$
$a = 5.3668 (5)$ Å	$D_x = 1.955$ Mg m^{-3}
$b = 10.6744 (8)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 8.4532 (6)$ Å	Cell parameters from 4015 reflections
$\beta = 102.772 (8)°$	$\theta = 3.8–29.9°$

$\mu = 3.37$ mm^{-1}

$T = 123$ K

Fragment cut from long rod, colourless

$0.6 \times 0.35 \times 0.15$ mm

Data collection

Oxford Diffraction Xcalibur E diffractometer	5854 measured reflections
Radiation source: sealed tube	2458 independent reflections
ω scans	2288 reflections with $I > 2\sigma(I)$
Absorption correction: analytical [CrysAlis PRO (Agilent, 2014), based on expressions derived by Clark & Reid (1995)]	$R_{int} = 0.039$
	$\theta_{max} = 29.9°$, $\theta_{min} = 3.8°$
	$h = -7 \rightarrow 7$
	$k = -14 \rightarrow 14$
$T_{min} = 0.286$, $T_{max} = 0.612$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.029$	
$wR(F^2) = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
2458 reflections	$(\Delta/\sigma)_{max} = 0.001$
117 parameters	$\Delta\rho_{max} = 0.87$ e Å^{-3}
7 restraints	$\Delta\rho_{min} = -0.65$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Refined as an inversion twin
	Absolute structure parameter: -0.07 (4)

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.

Refinement. Refined as a two-component inversion twin.

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

	x	y	z	U_{iso}*/U_{eq}
I1	0.36921 (6)	0.90844 (10)	0.91430 (3)	0.01907 (10)
O1	1.1192 (8)	0.5186 (4)	0.7440 (5)	0.0243 (10)
O2	0.8070 (8)	0.4561 (4)	0.5384 (5)	0.0258 (11)
H1H	0.936 (10)	0.415 (8)	0.516 (7)	0.031*
O3	0.8904 (9)	0.7986 (4)	0.5464 (5)	0.0282 (11)
O1W	1.1491 (15)	0.6160 (6)	1.1460 (9)	0.0274 (16)
H1W	1.253 (10)	0.553 (4)	1.143 (9)	0.033*
H2W	1.029 (9)	0.575 (5)	1.181 (8)	0.033*
N1	0.8348 (14)	0.6975 (7)	0.8380 (8)	0.0165 (16)
H3N	0.9372	0.6546	0.9205	0.025*
H1N	0.7172	0.7420	0.8773	0.025*
H2N	0.9315	0.7508	0.7926	0.025*
N2	0.5817 (11)	0.7743 (5)	0.3201 (6)	0.0224 (12)
H5N	0.428 (7)	0.740 (6)	0.277 (8)	0.027*
H4N	0.636 (13)	0.835 (5)	0.262 (7)	0.027*
C1	0.9010 (11)	0.5232 (5)	0.6669 (7)	0.0161 (12)
C2	0.7013 (12)	0.6073 (5)	0.7127 (7)	0.0155 (12)

H2	0.5882	0.5537	0.7640	0.019*
C3	0.5321 (12)	0.6737 (6)	0.5676 (7)	0.0177 (12)
H3A	0.4349	0.6100	0.4937	0.021*
H3B	0.4074	0.7271	0.6067	0.021*
C4	0.6816 (11)	0.7537 (6)	0.4743 (7)	0.0181 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01668 (17)	0.01986 (16)	0.01982 (16)	0.0013 (3)	0.00223 (11)	−0.0036 (2)
O1	0.018 (2)	0.029 (2)	0.024 (2)	0.009 (2)	−0.0010 (17)	−0.006 (2)
O2	0.016 (2)	0.031 (2)	0.029 (2)	0.0061 (18)	0.0031 (18)	−0.0140 (18)
O3	0.023 (3)	0.034 (3)	0.024 (2)	−0.011 (2)	−0.0023 (18)	0.011 (2)
O1W	0.025 (4)	0.022 (4)	0.034 (3)	−0.006 (3)	0.003 (3)	0.001 (3)
N1	0.013 (4)	0.019 (4)	0.018 (3)	0.007 (3)	0.005 (2)	0.001 (3)
N2	0.025 (3)	0.022 (3)	0.019 (3)	−0.003 (2)	0.002 (2)	0.002 (2)
C1	0.017 (3)	0.013 (3)	0.018 (3)	0.001 (2)	0.004 (2)	0.003 (2)
C2	0.015 (3)	0.015 (3)	0.016 (2)	−0.002 (2)	0.003 (2)	−0.001 (2)
C3	0.014 (3)	0.018 (3)	0.020 (3)	0.002 (3)	0.002 (2)	0.001 (2)
C4	0.016 (3)	0.016 (3)	0.022 (3)	0.002 (2)	0.004 (2)	0.001 (2)

Geometric parameters (Å, º)

O1—C1	1.209 (7)	N2—C4	1.314 (7)
O2—C1	1.305 (7)	N2—H5N	0.900 (14)
O2—H1H	0.876 (14)	N2—H4N	0.896 (14)
O3—C4	1.247 (7)	C1—C2	1.513 (8)
O1W—H2W	0.880 (14)	C2—C3	1.529 (8)
O1W—H1W	0.877 (14)	C2—H2	1.0000
N1—C2	1.492 (9)	C3—C4	1.509 (9)
N1—H3N	0.9100	C3—H3A	0.9900
N1—H1N	0.9100	C3—H3B	0.9900
N1—H2N	0.9100		
C1—O2—H1H	106 (5)	N1—C2—C3	112.1 (5)
H1W—O1W—H2W	98 (3)	C1—C2—C3	113.5 (5)
C2—N1—H3N	109.5	N1—C2—H2	107.7
C2—N1—H1N	109.5	C1—C2—H2	107.7
H3N—N1—H1N	109.5	C3—C2—H2	107.7
C2—N1—H2N	109.5	C4—C3—C2	113.1 (5)
H3N—N1—H2N	109.5	C4—C3—H3A	109.0
H1N—N1—H2N	109.5	C2—C3—H3A	109.0
C4—N2—H5N	118 (5)	C4—C3—H3B	109.0
C4—N2—H4N	124 (5)	C2—C3—H3B	109.0
H4N—N2—H5N	117 (7)	H3A—C3—H3B	107.8
O1—C1—O2	125.2 (6)	O3—C4—N2	123.1 (6)
O1—C1—C2	122.9 (5)	O3—C4—C3	119.1 (5)
O2—C1—C2	111.9 (5)	N2—C4—C3	117.8 (5)

N1—C2—C1	107.9 (5)		

O1—C1—C2—N1	12.5 (8)	N1—C2—C3—C4	64.3 (7)
O2—C1—C2—N1	−168.8 (5)	C1—C2—C3—C4	−58.3 (7)
O1—C1—C2—C3	137.5 (6)	C2—C3—C4—O3	−27.3 (8)
O2—C1—C2—C3	−43.9 (7)	C2—C3—C4—N2	153.8 (6)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*H*···O3ⁱ	0.88 (1)	1.71 (3)	2.549 (6)	160 (9)
N1—H1*N*···I1	0.91	2.65	3.528 (7)	164
N1—H2*N*···I1ⁱⁱ	0.91	2.89	3.591 (8)	135
N1—H2*N*···O3	0.91	2.11	2.766 (8)	129
N1—H3*N*···O1*W*	0.91	2.03	2.905 (6)	160
N2—H4*N*···I1ⁱⁱⁱ	0.90 (1)	3.07 (6)	3.659 (5)	125 (5)
N2—H4*N*···O1ⁱᵛ	0.90 (1)	2.37 (4)	3.171 (7)	149 (6)
N2—H5*N*···O1*W*ᵛ	0.90 (1)	2.12 (3)	2.983 (9)	160 (7)
O1*W*—H1*W*···I1ᵛⁱ	0.88 (1)	2.68 (2)	3.526 (8)	164 (5)
O1*W*—H2*W*···I1ᵛⁱⁱ	0.88 (1)	2.76 (4)	3.504 (7)	143 (6)

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