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D-Mannosamine hydrochloride (2-amino-2-deoxy-D-mannose hydrochloride): ionic hydrogen bonding in saccharides involving chloride and aminium ions

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D-Mannosamine hydrochloride (2-amino-2-deoxy-D-mannose hydrochloride), $C_6H_{14}NO_5^+ \cdot Cl^-$, (I), crystallized from a methanol/ethyl acetate/*n*-hexane solvent mixture at room temperature in a 4C_1 chair conformation that is slightly distorted towards the ${}^{C3,O5}B$ form. A comparison of the structural parameters of (I) with the corresponding parameters in α -D-glucosamine hydrochloride, (II), and β -D-galactosamine hydrochloride, (III)/(III'), was undertaken to evaluate the effects of ionic hydrogen bonding on structural properties. Three types of ionic hydrogen bonds are present in the crystals of (I)–(III)/(III'), *i.e.* $N^+ \cdots H \cdots O$, $N^+ \cdots H \cdots Cl^-$, and $O \cdots H \cdots Cl^-$. The exocyclic structural parameters in (I), (II), and (III)/(III') appear to be most influenced by this bonding, especially the exocyclic hydroxy groups, which adopt eclipsed conformations enabled by ionic hydrogen bonding to the chloride anion. Anomeric disorder was observed in crystals of (I), with an α : β ratio of 37:63. However, anomeric configuration appears to exert minimal structural effects; that is, bond lengths, bond angles, and torsion angles are essentially identical in both anomers. The observed disorder at the anomeric C atom of (I) appears to be caused by the presence of the chloride anion and atom O3 or O4 in proximal voids, which provide opportunities for hydrogen bonding to atom O1 in both axial and equatorial orientations.

1. Introduction

Ionic hydrogen bonds are hydrogen bonds that form between ions and molecules and have strengths in the range 5–35 kcal mol^{−1} (Mautner, 2005). Ionic hydrogen bonding occurs in ionic liquids (Pethes *et al.*, 2020) and has been implicated in biological processes, including enzyme catalysis and energetics (Yang & Castleman, 1991; Warshel & Russell, 1986). In serine proteases, for example, an anionic carboxylate side chain of an aspartic acid (Asp) residue is hydrogen bonded to the imidazole N atom of a histidine (His) residue in the catalytic triad to enhance the basicity of the imidazole ring (Warshel & Russell, 1986; Cleland *et al.*, 1998). Ionic hydrogen bonding is not commonly observed in saccharide crystal structures, which typically contain numerous conventional $O \cdots H \cdots O$ hydrogen bonds. The crystal structure of D-mannosamine hydrochloride (2-amino-2-deoxy-D-mannose hydrochloride), (I), provides an opportunity to evaluate ionic hydrogen bonding involving chloride anions and aminium cations. The crystal structure of (I) was determined and compared with those of two biologically-important amino-sugars, namely, α -D-glucosamine hydrochloride (2-amino-2-deoxy- α -D-glucose hydrochloride), (II) (Harrison *et al.*, 2007), and β -D-galactosamine hydrochloride (2-amino-2-deoxy- β -D-galactose hydrochloride), (III) and (III') (Takai *et al.*, 1972),

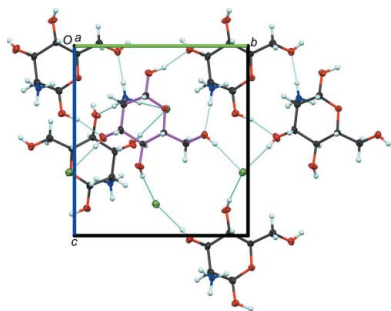


Table 1

Experimental details.

Crystal data	
Chemical formula	$C_6H_{14}NO_5^+ \cdot Cl^-$
M_r	215.63
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	120
a, b, c (Å)	8.3512 (4), 10.0750 (5), 11.0555 (6)
V (Å ³)	930.19 (8)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	3.65
Crystal size (mm)	0.28 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker PHOTON II
Absorption correction	Numerical (SADABS; Krause <i>et al.</i> , 2015)
T_{min}, T_{max}	0.462, 0.589
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19393, 1773, 1770
R_{int}	0.068
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.089, 1.22
No. of reflections	1773
No. of parameters	160
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.22, -0.25
Absolute structure	Flack x determined using 708 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.060 (10)

Computer programs: APEX3 (Bruker, 2018), SAINT (Bruker, 2018), SHELXT2014 (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), and Mercury (Macrae *et al.*, 2020).

with attention paid to the effects of ionic hydrogen bonding (*i.e.* $N^+ - H \cdots O$, $N^+ - H \cdots Cl^-$, and $O - H \cdots Cl^-$) on the structural parameters observed in these molecules. Knowledge of the latter effects could contribute to a better understanding of protein–saccharide and ion–saccharide binding interactions that are mediated by ionic hydrogen bonding (Kang *et al.*, 2020).

2. Experimental

2.1. Synthesis and crystallization

A powder sample of (I) was dissolved in a minimal volume of methanol, and ethyl acetate and *n*-hexane were added to give a final solution containing a 10:3:2 ratio of methanol, ethyl acetate, and *n*-hexane by volume. The resulting solution was left on a laboratory bench to allow the solvent to evaporate slowly at room temperature. Colorless block-like crystals of (I) formed in ~5 d.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Hydroxy and amine H atoms were located from a difference electron-density map and freely refined in cycles of least-squares refinement. All

other H atoms were included in geometrically calculated positions, with methine C–H = 1.00 Å and methylene C–H = 0.99 Å. H atoms on C atoms (methine and methylene) were refined with displacement parameters tied to that of the atom to which they are bonded [$U_{iso}(H) = 1.2U_{eq}(C)$]. The absolute configuration was determined from the known chirality of the molecule and by comparison of the Friedel pairs of reflections.

3. Results and discussion

Crystallization of D-mannosamine hydrochloride, (I) (Fig. 1), from a methanol/ethyl acetate/*n*-hexane solvent mixture gave crystals in the orthorhombic space group $P2_12_12_1$. The resulting structure revealed the presence of anomeric disorder, with an α -pyranose (αp): β -pyranose (βp) ratio of 37:63. This anomeric distribution compares favorably to that observed by ¹H NMR spectroscopy in aqueous solution (α : β ratio of 43:57), and supports prior conclusions that crystals of (I) contain a mixture of pyranose anomers (Horton *et al.*, 1966). Similar anomeric disorder has been observed in crystals of other reducing mono- and oligosaccharides, and has been attributed to crystal packing effects and/or to anomerization rates that are affected by crystallization conditions. Examples of cocrystallization include *N,N'*-diacetylchitobiose (αp : βp = 90:10; Mo & Jensen, 1978), lactose (αp : βp = 93:7; Fries *et al.*, 1971), melibiose (αp : βp = 80:20; Kanters *et al.*, 1976) and cellotetraose (αp : βp = 25:75; Gessler *et al.*, 1995). An evaluation of the electron-density map revealed that the crystal structures of the αp and βp forms of (I) are essentially degenerate, as indicated by the small atomic displacement ellipsoids shown in Fig. 1, and no residual electron density was observed that might indicate a displaced atom position. A rigid-body vibrations analysis based on the coordinates of (I) revealed negligible vibrational behavior of the pyranosyl rings and of the anomeric atoms O1 and O1A (Table S1 in the supporting information), indicating that the assignment of anomeric forms is correct and that structural differences between the two anomers under the cocrystallization conditions employed are negligible (Hirshfeld, 1976; Rosenfield *et al.*, 1978; Spek, 2020).

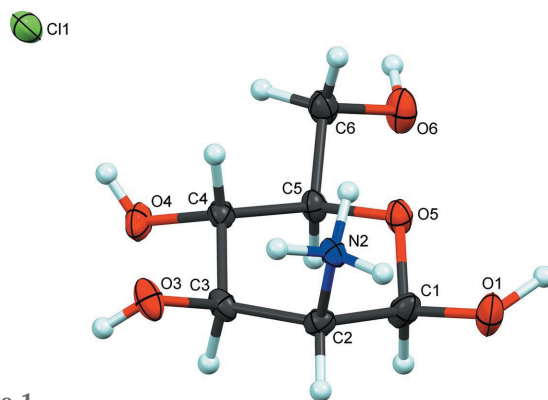


Figure 1

The molecular structure of (I), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The disordered (anomeric) region has been omitted for clarity. Only the β -anomer is shown.

Table 2
Cremer–Pople structural parameters for compounds (I)–(III)/(III').

Compound	ϕ (°)	θ (°)	Q (Å)	q_2	q_3
(I)	13.777	11.033	0.545	0.104	0.535
(II)	302.622	4.781	0.570	0.048	0.568
(III)	295.270	4.440	0.594	0.046	0.592
(III')	301.512	5.955	0.594	0.062	0.591

Cremer–Pople puckering parameters (Cremer & Pople, 1975) for (I) and for the structurally-related amino-sugars (II) and (III)/(III') (Fig. 2) reveal that all four aldopyranosyl rings adopt distorted 4C_1 conformations ($q_3 \gg q_2$) (Table 2). The degree of chair distortion varies, with (I) exhibiting the largest distortion ($\theta = 11^\circ$) and (III) the least ($\theta = 4^\circ$). The direction of distortion encoded in the value of ϕ differs in (I)–(III)/(III'), with (I) distorted towards $^3C_5O^5B$, and (II) and (III)/(III') distorted towards $B_{C2,C5}$.

Selected structural parameters in (I)–(III)/(III') are shown in Table 3. Differences in ring distortion (Table 2), the orientations and/or the conformations of the exocyclic substituents (*e.g.* $-\text{OH}$, $-\text{NH}_3^+$, and CH_2OH) (Table 3), and in hydrogen-bonding interactions (*e.g.* $\text{N}^+ - \text{H} \cdots \text{O}$, $\text{N}^+ - \text{H} \cdots \text{Cl}^-$, $\text{O} - \text{H} \cdots \text{O}$, and $\text{O} - \text{H} \cdots \text{Cl}^-$) complicate structural comparisons between (I)–(III)/(III'). Consequently, only relatively large differences in corresponding structural parameters in (I)–(III)/(III') are discussed below.

Differences in corresponding C–C bond lengths in (I)–(III)/(III') vary from 0.006 ($r_{\text{C3,C4}}$) to 0.029 Å ($r_{\text{C5,C6}}$). The C5–C6 bond lengths are typically the shortest C–C bonds in aldohexopyranosyl rings, and this trend is observed in (I), (II), and (III'), but not in (III). In (III), atom O6 is hydrogen bonded to Cl^- and serves as a dual acceptor to hydroxy H atoms in adjacent molecules in the lattice. In (III'), atom O6 serves as a donor to an O atom on an adjacent molecule, while serving as a mono-acceptor to a hydroxy H atom on an

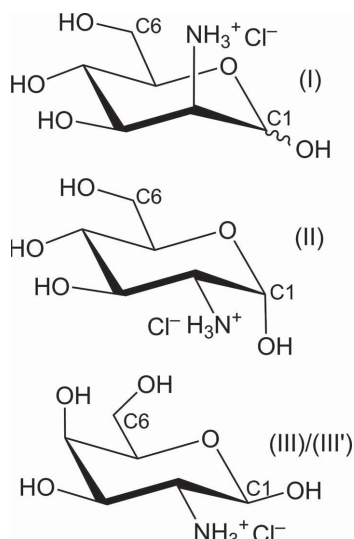


Figure 2
Chemical structures of D-mannosamine hydrochloride, (I), α -D-glucosamine hydrochloride, (II), and β -D-galactosamine hydrochloride, (III)/(III'). The numbering of the ring atoms in each structure is shown.

Table 3
Selected structural parameters (Å, °) in (I)–(III)/(III').

Parameter	Compound			
	(I)	(II)	(III) ^a	(III') ^a
C–C bond lengths (Å)				
C1–C2	1.516 (6)	1.527 (2)	1.523	1.532
C2–C3	1.525 (5)	1.525 (2)	1.515	1.519
C3–C4	1.527 (5)	1.528 (2)	1.528	1.522
C4–C5	1.526 (6)	1.528 (2)	1.517	1.522
C5–C6	1.499 (6)	1.515 (2)	1.525	1.496
C–O bond lengths (Å)				
C1–O1	1.394 (6)/ 1.394 (11)	1.390 (2)	1.390	1.398
C1–O5	1.420 (5)	1.422 (2)	1.435	1.429
C3–O3	1.422 (5)	1.431 (2)	1.426	1.428
C4–O4	1.428 (5)	1.424 (2)	1.447	1.453
C5–O5	1.449 (4)	1.442 (2)	1.446	1.441
C6–O6	1.435 (5)	1.415 (2)	1.427	1.447
C–N bond lengths (Å)				
C2–N2	1.486 (6)	1.490 (2)	1.504	1.503
Bond angles (°)				
C1–C2–C3	110.6 (3)	112.6 (1)	111.2	111.7
C2–C3–C4	113.9 (3)	109.7 (1)	109.2	109.7
C3–C4–C5	111.6 (3)	109.6 (1)	108.1	108.0
C4–C5–O5	109.9 (3)	109.0 (1)	110.5	109.4
C5–O5–C1	112.6 (3)	114.1 (1)	110.1	111.1
O5–C1–C2	109.8 (3)	109.2 (1)	110.7	109.7
C4–C5–C6	111.8 (3)	113.5 (1)	110.2	112.0
Torsion angles (°) ^b				
C1–C2–C3–C4	−46.1 (4)	−51.6 (2)	−53.8	−52.6
C2–C3–C4–C5	44.2 (4)	53.6 (2)	56.0	55.6
C3–C4–C5–O5	−50.4 (4)	−58.5 (2)	−61.8	−62.1
C4–C5–O5–C1	62.8 (4)	63.5 (2)	64.3	66.0
C5–O5–C1–C2	−65.5 (4)	−59.8 (2)	−60.1	−60.8
O5–C1–C2–C3	55.2 (4)	53.1 (2)	55.8	54.3
C2–C1–O1–H	−154 (11)/ −170 (13)	−163.2	143.9	149.3
C1–C2–N2–H _A	43 (3)	52.9	53.3	53.6
C1–C2–N2–H _B	−71 (3)	−67.1	−53.3	−59.2
C1–C2–N2–H _C	167 (4)	173	−177.0	174.5
C2–C3–O3–H	−141 (6)	55.7	−125.4	−135.7
C3–C4–O4–H	128 (5)	−64.1	−107.3	−98.2
C3–C4–C5–C6	−167.6 (3)	−177.0 (1)	178.5	176.7
C4–C5–C6–O6	−169.4 (3) (<i>gt</i>)	62.1 (2) (<i>gg</i>)	−170.6 (<i>gt</i>)	−167.3 (<i>gt</i>)
C5–C6–O6–H	163 (5)	−78.5	178.3	−98.8

Notes: (a) s.u. values were not reported in the original article. (b) Definitions of the *gg* (*gauche–gauche*), *gt* (*gauche–trans*), and *tg* (*trans–gauche*) conformers of the exocyclic hydroxymethyl groups in (I)–(III)/(III') are as follows: *gg*, H5 *anti* to O6; *gt*, C4 *anti* to O6; *tg*, O5 *anti* to O6.

adjacent molecule. Ionic hydrogen bonding involving atom O6 in (III) appears to lengthen the C5–C6 bond relative to the same bond in (III'), while $r_{\text{C6,O6}}$ is shorter in (III) than in (III'). Since the conformations of the exocyclic hydroxymethyl group in (III) and (III') are identical (*gt*), any effects on $r_{\text{C5,C6}}$ and $r_{\text{C6,O6}}$ that might be caused by this factor are probably small. While atom O6 in (I) is also hydrogen bonded to Cl^- , as observed in (III), the hydrogen-bond acceptor behavior of O6 in (I) differs significantly from that observed in (III), such that differences in $r_{\text{C5,C6}}$ and $r_{\text{C6,O6}}$ between the two structures cannot be interpreted reliably in structural terms (see discussion below).

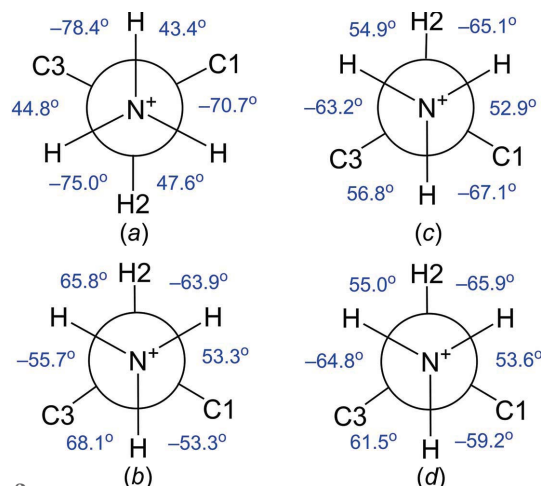


Figure 3

Newman projections for the C2–N2 bond, showing the H–N2–C2–H2/C1/C3 torsion angles (in blue) involving the N–H hydrogens of the NH_3^+ substituent in (a) (I), (b) (II), (c) (III), and (d) (III'). The four rotamers approximate idealized staggered conformations about the C2–N2 bond.

The C1–O1 bonds in (I)–(III)/(III') are the shortest exocyclic C–O bonds in all four structures (1.390–1.398 Å) (Table 3). The endocyclic C1–O5 bonds are consistently shorter than the endocyclic C5–O5 bonds in all cases, although the difference between these bond lengths may be slightly greater in α -anomers (I) and (II) than in β -anomers (III)/(III'). Torsion angles involving exocyclic C–O bonds are expected to influence exocyclic $r_{\text{C,O}}$ in that, as a given C–O rotamer becomes more eclipsed, the associated C–O bond is expected to lengthen. The significant variability observed in these torsion angles in (I)–(III)/(III') contributes to the observed differences in the C–O bond lengths, superimposed on contributions made from different hydrogen bonding involving the hydroxy O atoms and their associated H atoms, and different C–O bond orientations in the ring (axial *versus* equatorial).

The exocyclic C2–N2 bonds in (I)–(III)/(III') range from 1.486 Å in (I) to 1.504 Å in (III), and these bonds are ~ 0.06 Å longer than the exocyclic C3–O3 and C4–O4 bonds in these structures (1.422–1.453 Å). There is no discernible dependence of $r_{\text{C}_2\text{N}_2}$ on C2–N2 bond orientation [*e.g.* $r_{\text{C}_2\text{N}_2}$ in (I) and (III) are essentially identical], although this comparison is complicated due to different hydrogen-bonding behavior involving the NH_3^+ groups in these structures.

Three types of endocyclic bond angles are found in (I)–(III)/(III'), namely, C–C–C, C–C–O, and C–O–C. The C–C–C bond angles are in the range 108.0–113.9° (average: 110.5°), the C–C–O bond angles are in the range 109.0–110.7° (average: 109.8°), and the C–O–C bond angles are in the range 110.1–114.1° (average: 112.0°). The exocyclic C4–C5–C6 bond angles in (I)–(III)/(III') range from 110.2 to 113.5° (average: 111.9°) and are comparable to, if not slightly larger than, the endocyclic C–C–C bond angles.

The six endocyclic torsion angles in (I)–(III)/(III') involving heavy atoms are in the range 44–66° (absolute values), with the larger torsion angles associated with the C4–C5–O5–

C1 and C5–O5–C1–C2 pathways (Table 3). The conformation about the C2–N2 bonds in (I)–(III)/(III') is nearly ideal, with the three N–H hydrogens yielding torsion angles of 43–78° (absolute values) with respect to the C1, H2, and C3 substituents attached to C2 (Fig. 3). This behavior contrasts with that observed for the C–C–O–H torsion angles involving the ring C atoms: C2–C1–O1–H, C2–C3–O3–H, and C3–C4–O4–H (Fig. 4). While prior work has shown that the uncertainties in C–C–O–H torsion angles obtained from conventional X-ray crystallography are large (± 3 – 4° ; Meredith *et al.*, unpublished), the results nevertheless reveal conformations that are nearly eclipsed in (I) and (III)/(III'), although less so in (II). Clearly, in the crystalline state, it is energetically favorable for C–C–O–H torsion angles to deviate from those associated with staggered rotamers, consistent with the low barriers of C–O bond rotation leading to these torsion-angle deformations (Wu & Houk, 1990; Anderson, 1996). Under these conditions, crystal packing forces, such as intra- and intermolecular hydrogen bonding and steric factors, among others, conspire to produce solid-state geometries that might otherwise be less favored in

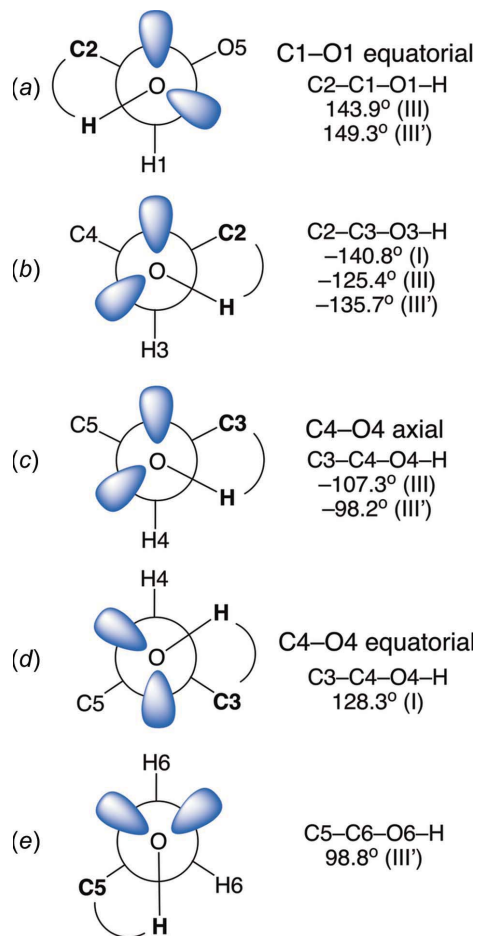


Figure 4

Newman projections for the (a) C1–O1, (b) C3–O3, (c)/(d) C4–O4, and (e) C5–O6 bonds in (I) and (III)/(III'), and the observed torsion angles involving hydroxy H atoms in (I), (III), and (III'), corresponding to the near-eclipsed rotamers observed in the crystal structures. Standard uncertainties for the distances can be found in Table 4.

solution. In the present cases, ionic hydrogen bonding involving either Cl^- as an acceptor or N^+-H hydrogens as donors (see discussion below) adds to the ensemble of more common modes of hydrogen bonding (*i.e.* $\text{O}-\text{H}\cdots\text{O}$) to determine exocyclic torsional properties in the crystals.

The exocyclic hydroxymethyl groups in (I), (III), and (III') adopt the *gt* conformation (C4 anti to O6), with an average $\text{C4}-\text{C5}-\text{C6}-\text{O6}$ torsion angle of $-169.1 \pm 1.7^\circ$ (Table 3). The hydroxymethyl group in (II) adopts the *gg* conformation (H5 anti to O6), with a $\text{C4}-\text{C5}-\text{C6}-\text{O6}$ torsion angle of 62.1° . These conformers are commonly observed in gluco- and galactopyranosyl rings in aqueous solution based on the interpretation of $^3J_{\text{H5,H6R}}$ and $^3J_{\text{H5,H6S}}$ values measured by NMR spectroscopy (Bock & Duus, 1994; Rockwell & Grindley, 1998; Thibaudeau *et al.*, 2004).

A key feature in the crystal structure of (I) is the presence of ionic hydrogen bonding involving the chloride anion as an acceptor, or the protonated amino N atom as a donor. Conventional intra- and intermolecular hydrogen bonding in saccharide crystal structures typically involves O atoms as donors and/or acceptors, with electron density provided by two localized pairs of unshared electrons. This arrangement dictates the maximum number of hydrogen bonds in which the O atoms participate. The electronic structure of Cl^- is $1s^2 2s^2 2p^6 3s^2 3p^6$ (18 electrons), and the valence electrons reside in $3s$ and $3p$ orbitals. However, unlike oxygen, the outer electron density is not localized in Cl^- , but rather distributes over the 'surface' of the anion. Consequently, Cl^- can serve as an acceptor in up to six or seven hydrogen bonds, and the orientations of these bonds around the anion are not specific (Pethes *et al.*, 2020). Bearing these facts in mind, the Cl^- anion in (I) participates as an acceptor in four hydrogen bonds. Three donors are contributed by atoms O3 , O4 , and O6 in

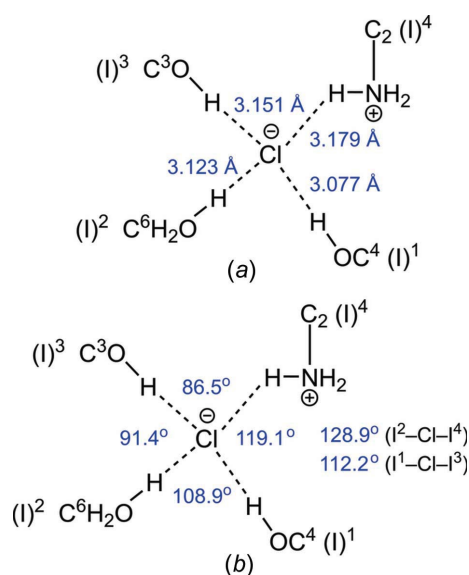


Figure 5
Ionic hydrogen bonding involving the chloride anion of (I) and four donors on different molecules of (I) in the crystalline lattice [shown as (I)^{1–4}]. (a) Four hydrogen-bond lengths measured from the Cl^- anion to the donor heavy atoms O or N. (b) Six bond angles around Cl^- measured from the donor heavy atoms.

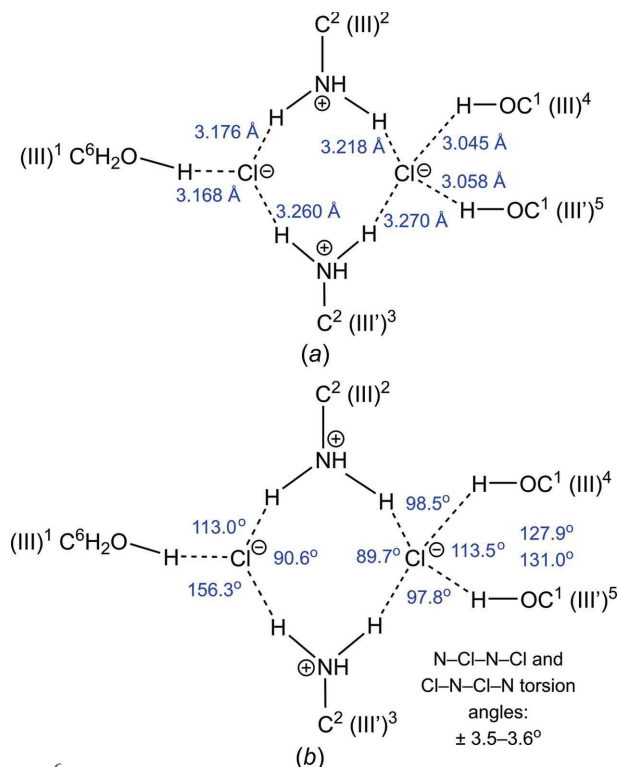


Figure 6

The two different types of ionic hydrogen bonding to Cl^- in the crystalline lattice of (III)/(III') involving three and four donors supplied by five different molecules of (III)/(III') [labeled (III)/(III')^{1–5}]. Amino groups on two different molecules each serve as two donors to two different Cl^- anions. The two Cl^- anions, two donor N atoms, and donor O atom supplied by atom C6 are essentially coplanar. (a) Hydrogen-bond lengths measured from Cl^- to the donor heavy atoms. (b) Bond angles around both Cl^- anions in the lattice measured from the donor heavy atoms.

three different molecules of (I). The fourth donor is provided by an NH_3^+ group in a fourth molecule of (I). Some structural details of these interactions are shown in Fig. 5. Internuclear distances between Cl^- and the donor heavy atoms are in the range 3.1–3.2 Å [Fig. 5(a)], in contrast with a distance of ~ 2.8 Å for $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding. In addition, although not shown in Fig. 5, the $\text{N}^+-\text{H}\cdots\text{Cl}^-$ and $\text{O}-\text{H}\cdots\text{Cl}^-$ hydrogen-bond angles of $153-173^\circ$ are consistent with geometries associated with hydrogen bonding (Pethes *et al.*, 2020). The hydrogen-bond length involving the N-atom donor [3.179 (4) Å] does not appear to differ appreciably from those involving the O-atom donors [3.077 (3)–3.151 (3) Å]. The plasticity of the bonding geometry around Cl^- is illustrated in Fig. 5(b), where $\text{X}\cdots\text{Cl}^-\cdots\text{Y}$ bond angles between the heavy atoms X and Y range from 86.49 (9) to 128.90 (10)°. In principle, Cl^- could accommodate two–three more hydrogen bonds in the crystalline lattice of (I), but presumably the steric bulk imposed by multiple molecules of (I) clustered around the anion precludes a larger number of hydrogen bonds, although ostensibly additional donors could be provided by small solvent molecules like water. The ionic hydrogen-bonding motifs in (I) and (II) are very similar. For example, in (II), Cl^- participates in four hydrogen bonds involving atoms O1 , O3 , and O4 , and the NH_3^+ group as

Table 4
Hydrogen-bond geometry in (I)–(III') (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
Compound (I)				
$O1-H1O\cdots O3^{iii}$	0.94 (17)	1.88 (17)	2.785 (6)	160 (14)
$O1A-H1OA\cdots Cl1^{iv}$	0.90 (18)	2.70 (18)	3.247 (9)	120 (12)
$O1A-H1OA\cdots O4^{iv}$	0.90 (18)	2.15 (17)	3.017 (10)	160 (15)
$N2-H2NB\cdots O6^v$	0.84 (4)	1.92 (4)	2.762 (4)	172 (4)
$N2-H2NC\cdots O4^{vi}$	0.90 (6)	2.11 (6)	2.960 (5)	157 (5)
$N2-H2NA\cdots Cl1^{vii}$	0.98 (6)	2.27 (6)	3.179 (4)	153 (4)
$O3-H3O\cdots Cl1^i$	0.78 (8)	2.38 (8)	3.151 (3)	173 (7)
$O4-H4O\cdots Cl1$	0.79 (6)	2.29 (6)	3.077 (3)	172 (6)
$O6-H6O\cdots Cl1^{ii}$	0.81 (6)	2.33 (6)	3.123 (3)	171 (6)
Compound (II)				
$N2-H2A\cdots O6^i$	0.89	1.89	2.777 (17)	172
$N2-H2B\cdots O4^{ii}$	0.89	2.15	2.893 (19)	141
$N2-H2C\cdots Cl1^{iii}$	0.89	2.38	3.174 (13)	149
$O1-H1O\cdots Cl1^{iv}$	0.82	2.35	3.145 (12)	162
$O3-H3O\cdots Cl1^v$	0.84	2.35	3.191 (14)	173
$O4-H4O\cdots Cl1$	0.82	2.35	3.167 (14)	175
$O6-H6O\cdots O3^v$	0.81	1.95	2.737 (17)	163
Compound (III)				
$O1-H1O\cdots Cl2^i$	0.98	2.11	3.045	159
$N2-H2A\cdots O3^{ii}$	0.92	2.08	2.980	166
$N2-H2B\cdots Cl1^{iii}$	0.95	2.23	3.176	170
$N2-H2C\cdots Cl2^{iii}$	0.91	2.34	3.218	162
$O3-H3O\cdots O4^{iii}$	0.87	2.02	2.865	164
$O4-H4O\cdots O6^{iv}$	0.88	2.02	2.896	176
$O6-H6O\cdots Cl1^v$	0.89	2.31	3.168	161
$O1'-H1'O\cdots Cl2$	0.88	2.18	3.058	175
$N2'-H2'A\cdots O3^{vi}$	0.90	2.13	2.937	150
$N2'-H2'B\cdots Cl1$	0.95	2.32	3.260	170
$N2'-H2'C\cdots Cl2^{vi}$	0.90	2.45	3.270	151
$O3'-H3'O\cdots O4^{iii}$	0.77	2.32	3.073	165
$O4'-H4'O\cdots O6^{vii}$	0.96	1.78	2.733	175
$O6'-H6'O\cdots O6^i$	0.89	2.01	2.847	156

Symmetry codes for (I): (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$. Symmetry codes for (II): (i) $-x, y+\frac{1}{2}, -z+2$; (ii) $-x+1, y+\frac{1}{2}, -z+2$; (iii) $x, y, z+1$; (iv) $x-1, y, z$; (v) $-x+1, y-\frac{1}{2}, -z+2$. Symmetry codes for (III): (i) $x-\frac{1}{2}, -y-\frac{1}{2}, -z-1$; (ii) $-x-\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $-x, y+\frac{1}{2}, -z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (v) $x+1, y, z$; (vi) $x-\frac{1}{2}, -y-\frac{1}{2}, -z$; (vii) $x+\frac{1}{2}, -y-\frac{1}{2}, -z-1$.

donors. In (II), atom O1 replaces O6 in (I) as the third O-atom donor. Hydrogen-bond lengths (3.145–3.191 Å) and angles (85.5–130.0°) observed in (II) are similar to those observed in (I). On the other hand, ionic hydrogen bonding in (III)/(III') differs significantly from that observed in (I) and (II) (Fig. 6). Two Cl^- anions are hydrogen bonded to two NH_3^+ bridges, with one Cl^- anion participating in three hydrogen bonds and the other participating in four. The hydrogen-bond lengths in (III)/(III') and the bonding geometry about the latter Cl^- anion are very similar to those observed in (I) and (II). For the former Cl^- anion, the sum of the bond angles involving the donor heavy atoms (113.0 + 156.3 + 90.6°) is 359.9°, which is very close to 360° and indicates that the Cl^- anion and the three donor heavy atoms are essentially coplanar. The largest deviation from the mean plane of the aminium–chloride hydrogen-bonded 'ring' formed by the two N and Cl atoms in (III)/(III') is 0.051 Å, and the $Cl\cdots N-H$ angles range from 6.73 to 20.99°, providing further evidence that this 'ring' is essentially planar. Thus, the two Cl^- anions, the two donor N atoms and the O-atom donor provided by C6 are coplanar. These results show that the hydrogen-bonding structure

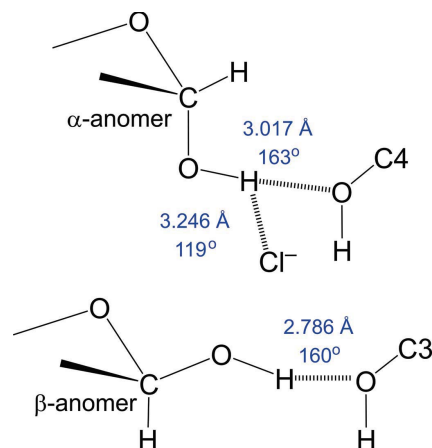


Figure 7

Hydrogen bonding involving the anomeric hydroxy group in the α - and β -anomers of (I). In each structure, the internuclear distance between the heavy atoms and the $O-H\cdots O$ or $O-H\cdots Cl^-$ pseudo-hydrogen-bond angle are shown.

around Cl^- can vary widely, with the present work providing examples of a trigonal planar geometry and a geometry resembling that found around a distorted tetrahedral C atom. These saccharide-based models of Cl^- hydrogen bonding may provide useful insights into non-bonded interactions that occur in Cl^- -containing ionic liquids and concentrated aqueous chloride salt solutions (Petthes *et al.*, 2020), and during saccharide–receptor binding mediated by a bound Cl^- anion.

Two ionic hydrogen bonds of the type $N^+-H\cdots O$ are observed in (I). One involves an O6 acceptor on an adjacent molecule and has an $N2\cdots O6^v$ distance of 2.762 (4) Å and an $N^+-H\cdots O$ angle of 172 (4)°. The second hydrogen bond

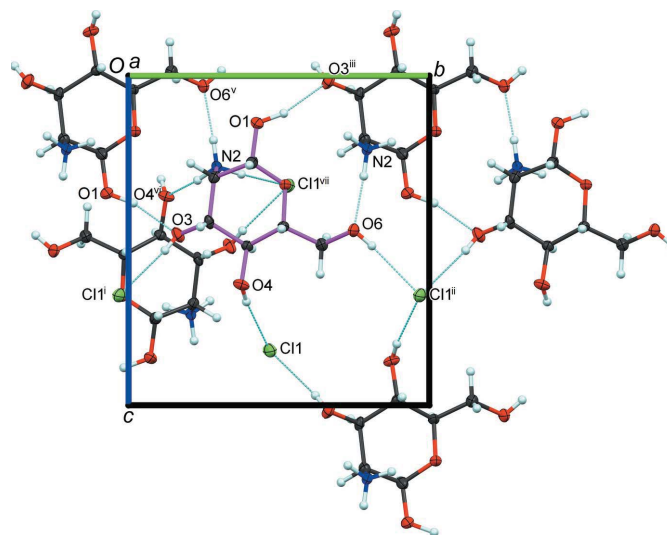


Figure 8

Packing diagram of (Ib), viewed along the a axis. The magenta-colored sugar molecule represents the reference asymmetric unit and the light-blue dashed bonds identify the hydrogen bonds. Atoms involved in hydrogen bonding are labeled for clarity. The minor α -anomer (disordered region) has been omitted for clarity. [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$.]

involves an O4 acceptor on an adjacent molecule and has a length of 2.961 (5) Å and an $N^+-H\cdots O$ angle of 157 (5)°. In (II), one $N^+-H\cdots O$ hydrogen bond is observed to O6 on an adjacent molecule, with a distance of 2.777 Å and an $N^+-H\cdots O$ angle of 172°. An additional interaction with the N atom is observed involving atom O4 (2.893 Å) in an adjacent molecule, but this interaction is likely to be weak due to an unfavorable angle of 141°. In (III), one $N^+-H\cdots O$ hydrogen bond is observed to atom O3 on an adjacent molecule, with a bond length of 2.980 Å and an angle of 166°, while in (III'), a single $N^+-H\cdots O$ hydrogen bond is observed to atom O3 on an adjacent molecule with a bond length of 2.937 Å and an angle of 150°. Collectively, ionic hydrogen-bond lengths involving N^+-H donors do not differ appreciably in length from those found for $O-H\cdots O$ hydrogen bonds, but in some cases the interactions are probably weak due to non-optimal $N^+-H\cdots O$ hydrogen-bond angles.

The X-ray structure of (I) contains anomeric disorder in that both anomers are present in the crystal in an $\alpha:\beta$ ratio of approximately 37:63. Both anomers are accommodated in the lattice, presumably because hydrogen-bond acceptors reside near the anomeric hydroxy group regardless of whether the C1—O1 bond is axial (α) or equatorial (β) (Fig. 7). In both anomers, hydrogen bonding to the anomeric hydroxy group is observed, with the hydroxy group serving only as a donor. For the α -anomer, the acceptors are atom O4 on an adjacent molecule and Cl^- , whereas for the β -anomer, O3 of an adjacent molecule is the sole acceptor. The strengths of this hydrogen bonding probably differ, with that in the β -anomer likely to be stronger given the shorter $O\cdots O$ internuclear

distance (Fig. 7). These differences may play a role in determining the anomeric ratio, with the β -anomer in greater abundance than the α -anomer by a factor of ~ 1.7 .

The extended structure of (I), considering only the major β -anomer, is formed by seven hydrogen-bond contacts (Fig. 8 and Table 4). The Cl atom serves as a four-coordinate acceptor for hydrogen bonds from four different neighboring D-mannosamine molecules consisting of the amine N atom, O3, O4, and O6. The amine N atom, predictably, is a donor in three hydrogen bonds, *i.e.* to Cl^{1viii} , and $O4^{vi}$, and $O6^v$ on two other neighboring molecules (see Table 4 for symmetry codes). Hydroxy atom O1 acts only as a donor with a hydrogen bond to $O3^{iii}$. Hydroxy atoms O3, O4, and O6 are both acceptors and donors. In contrast, for the α -anomer, atom O1A forms a hydrogen bond to $O4^{iv}$, removing the O1 contact to O3 (Fig. 9). There is also a weak, poorly directional, contact to the Cl atom from O1A that is still within a typical hydrogen-bond contact range. Presumably, the α -anomer is accommodated in the lattice through the formation of an additional, if slightly weaker, hydrogen bond. The overall packing can be viewed as hydrogen-bonded sheets of D-mannosamine and Cl atoms in layers that are parallel to the *bc* plane. The three-dimensional framework is generated *via* contacts from the amine group to atoms O4 and Cl1 across the sheets.

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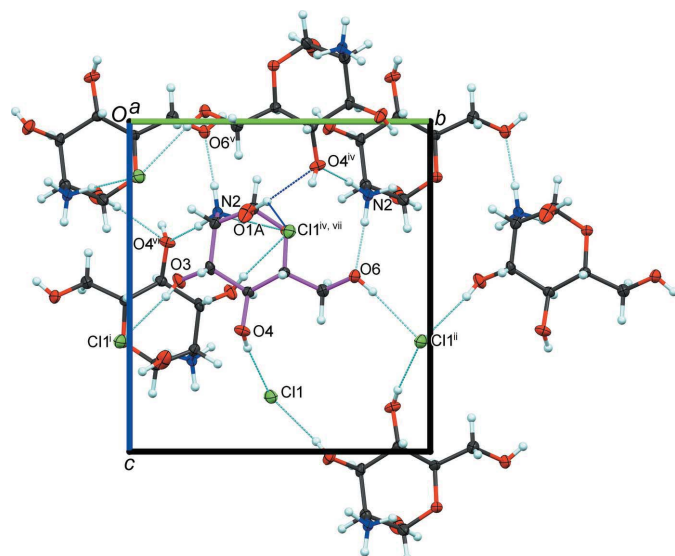


Figure 9

Packing diagram of (Ia), viewed along the *a* axis. The magenta-colored sugar molecule represents the reference asymmetric unit and the light-blue dashed bonds identify the hydrogen bonds. The bifurcated hydrogen bonds in the anomeric region of the minor α -anomer are highlighted in the dark-blue dashed bonds. Atoms involved in hydrogen bonding are labeled for clarity. The major β -anomer in the disordered anomeric region has been omitted to clarify the interactions of the minor α -anomer. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$.]

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supporting information

Acta Cryst. (2022). **C78**, 223–230 [https://doi.org/10.1107/S2053229622002121]

D-Mannosamine hydrochloride (2-amino-2-deoxy-D-mannose hydrochloride): ionic hydrogen bonding in saccharides involving chloride and aminium ions

Jieye Lin, Allen G. Oliver and Anthony S. Serianni

Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b).

2-Amino-2-deoxy-D-mannose hydrochloride

Crystal data

$\text{C}_6\text{H}_{14}\text{NO}_5^+\cdot\text{Cl}^-$

$M_r = 215.63$

Orthorhombic, $P2_12_12_1$

$a = 8.3512$ (4) Å

$b = 10.0750$ (5) Å

$c = 11.0555$ (6) Å

$V = 930.19$ (8) Å³

$Z = 4$

$F(000) = 456$

$D_x = 1.540$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 9972 reflections

$\theta = 5.9\text{--}70.4^\circ$

$\mu = 3.65$ mm⁻¹

$T = 120$ K

Block, colorless

$0.28 \times 0.20 \times 0.18$ mm

Data collection

Bruker PHOTON II
diffractometer

Radiation source: Ius micro-focus

Detector resolution: 7.41 pixels mm⁻¹

ω and ϕ -scans

Absorption correction: numerical
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.462$, $T_{\max} = 0.589$

19393 measured reflections

1773 independent reflections

1770 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 70.5^\circ$, $\theta_{\min} = 5.9^\circ$

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.089$

$S = 1.22$

1773 reflections

160 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 1.3591P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.22$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Absolute structure: Flack x determined using
708 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.060 (10)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.62782 (14)	0.46942 (10)	0.83365 (9)	0.0272 (3)	
O1	0.4210 (7)	0.4273 (5)	0.1434 (4)	0.0275 (16)	0.628 (11)
H1O	0.418 (19)	0.515 (17)	0.114 (14)	0.12 (6)*	0.628 (11)
O1A	0.2130 (11)	0.3879 (10)	0.2779 (9)	0.036 (3)	0.372 (11)
H1OA	0.16 (2)	0.452 (16)	0.241 (14)	0.05 (4)*	0.372 (11)
O3	0.5395 (4)	0.1644 (3)	0.4828 (3)	0.0235 (7)	
H3O	0.494 (9)	0.122 (7)	0.531 (7)	0.06 (2)*	
O4	0.3977 (4)	0.3747 (3)	0.6342 (3)	0.0227 (7)	
H4O	0.460 (7)	0.391 (6)	0.686 (5)	0.034 (16)*	
O5	0.4320 (3)	0.5213 (3)	0.3310 (2)	0.0192 (6)	
O6	0.3460 (4)	0.7488 (3)	0.4689 (3)	0.0272 (7)	
H6O	0.360 (8)	0.810 (6)	0.514 (5)	0.034 (14)*	
N2	0.6321 (5)	0.2938 (3)	0.2770 (3)	0.0162 (7)	
H2NC	0.690 (6)	0.232 (5)	0.316 (5)	0.032 (14)*	
H2NB	0.631 (5)	0.285 (4)	0.201 (4)	0.006 (9)*	
H2NA	0.673 (6)	0.383 (6)	0.295 (4)	0.030 (14)*	
C1	0.3767 (6)	0.4101 (4)	0.2640 (4)	0.0224 (8)	
H1	0.257820	0.401209	0.271205	0.027*	0.628 (11)
H1A	0.401375	0.423626	0.176312	0.027*	0.372 (11)
C2	0.4593 (5)	0.2851 (4)	0.3081 (3)	0.0172 (8)	
H2	0.411714	0.206877	0.265613	0.021*	
C3	0.4359 (5)	0.2680 (4)	0.4440 (3)	0.0167 (8)	
H3	0.323017	0.238937	0.458421	0.020*	
C4	0.4651 (5)	0.3944 (4)	0.5169 (3)	0.0157 (8)	
H4	0.582936	0.409874	0.524592	0.019*	
C5	0.3873 (5)	0.5150 (4)	0.4575 (3)	0.0167 (8)	
H5	0.268152	0.508716	0.464874	0.020*	
C6	0.4445 (6)	0.6424 (4)	0.5127 (4)	0.0217 (9)	
H6A	0.437407	0.637221	0.601987	0.026*	
H6B	0.557658	0.658379	0.490346	0.026*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0383 (5)	0.0222 (5)	0.0212 (4)	−0.0120 (5)	0.0001 (5)	0.0021 (4)

O1	0.046 (3)	0.021 (3)	0.016 (3)	0.007 (2)	−0.004 (2)	0.0019 (18)
O1A	0.033 (5)	0.030 (5)	0.044 (6)	0.015 (4)	−0.026 (4)	−0.010 (4)
O3	0.0240 (15)	0.0191 (14)	0.0273 (16)	0.0069 (13)	0.0075 (13)	0.0079 (13)
O4	0.0245 (16)	0.0300 (16)	0.0135 (13)	−0.0005 (13)	0.0023 (12)	0.0053 (12)
O5	0.0286 (14)	0.0154 (13)	0.0135 (12)	0.0019 (11)	0.0022 (11)	0.0002 (12)
O6	0.045 (2)	0.0156 (14)	0.0209 (14)	0.0106 (15)	−0.0004 (14)	−0.0013 (12)
N2	0.0181 (17)	0.0140 (16)	0.0165 (16)	0.0013 (14)	−0.0003 (15)	0.0025 (12)
C1	0.029 (2)	0.0185 (19)	0.0197 (18)	0.0055 (18)	−0.0071 (19)	−0.0032 (15)
C2	0.0171 (19)	0.0154 (18)	0.0192 (19)	0.0011 (15)	−0.0020 (15)	−0.0023 (15)
C3	0.0150 (18)	0.0124 (18)	0.023 (2)	0.0033 (15)	0.0035 (15)	0.0030 (16)
C4	0.0150 (18)	0.0172 (18)	0.0150 (18)	−0.0012 (15)	0.0019 (15)	0.0015 (15)
C5	0.0210 (19)	0.0152 (17)	0.0140 (16)	0.0021 (16)	0.0025 (15)	0.0011 (14)
C6	0.029 (2)	0.017 (2)	0.020 (2)	0.0000 (17)	0.0002 (17)	0.0011 (16)

Geometric parameters (Å, °)

O1—C1	1.394 (6)	N2—H2NA	0.98 (6)
O1—H1O	0.94 (17)	C1—C2	1.516 (5)
O1A—C1	1.394 (11)	C1—H1	1.0000
O1A—H1OA	0.90 (18)	C1—H1A	1.0000
O3—C3	1.422 (5)	C2—C3	1.525 (5)
O3—H3O	0.78 (8)	C2—H2	1.0000
O4—C4	1.428 (5)	C3—C4	1.527 (5)
O4—H4O	0.79 (6)	C3—H3	1.0000
O5—C1	1.420 (5)	C4—C5	1.526 (5)
O5—C5	1.448 (4)	C4—H4	1.0000
O6—C6	1.435 (5)	C5—C6	1.500 (5)
O6—H6O	0.81 (6)	C5—H5	1.0000
N2—C2	1.487 (5)	C6—H6A	0.9900
N2—H2NC	0.90 (6)	C6—H6B	0.9900
N2—H2NB	0.84 (4)		
C1—O1—H1O	116 (9)	C1—C2—H2	108.8
C1—O1A—H1OA	111 (10)	C3—C2—H2	108.8
C3—O3—H3O	108 (5)	O3—C3—C2	107.6 (3)
C4—O4—H4O	112 (4)	O3—C3—C4	110.9 (3)
C1—O5—C5	112.7 (3)	C2—C3—C4	113.9 (3)
C6—O6—H6O	106 (4)	O3—C3—H3	108.1
C2—N2—H2NC	112 (3)	C2—C3—H3	108.1
C2—N2—H2NB	102 (3)	C4—C3—H3	108.1
H2NC—N2—H2NB	114 (4)	O4—C4—C5	109.5 (3)
C2—N2—H2NA	110 (3)	O4—C4—C3	107.5 (3)
H2NC—N2—H2NA	110 (4)	C5—C4—C3	111.7 (3)
H2NB—N2—H2NA	108 (4)	O4—C4—H4	109.4
O1—C1—O5	108.3 (4)	C5—C4—H4	109.4
O1A—C1—O5	112.8 (5)	C3—C4—H4	109.4
O1—C1—C2	106.9 (4)	O5—C5—C6	105.9 (3)
O1A—C1—C2	106.1 (5)	O5—C5—C4	109.9 (3)

O5—C1—C2	109.8 (3)	C6—C5—C4	111.7 (3)
O1—C1—H1	110.6	O5—C5—H5	109.8
O5—C1—H1	110.6	C6—C5—H5	109.8
C2—C1—H1	110.6	C4—C5—H5	109.8
O1A—C1—H1A	109.4	O6—C6—C5	108.6 (3)
O5—C1—H1A	109.4	O6—C6—H6A	110.0
C2—C1—H1A	109.4	C5—C6—H6A	110.0
N2—C2—C1	108.6 (3)	O6—C6—H6B	110.0
N2—C2—C3	111.0 (3)	C5—C6—H6B	110.0
C1—C2—C3	110.7 (3)	H6A—C6—H6B	108.3
N2—C2—H2	108.8		
C5—O5—C1—O1	178.1 (4)	O3—C3—C4—O4	−74.2 (4)
C5—O5—C1—O1A	52.6 (6)	C2—C3—C4—O4	164.3 (3)
C5—O5—C1—C2	−65.5 (4)	O3—C3—C4—C5	165.7 (3)
O1—C1—C2—N2	50.3 (5)	C2—C3—C4—C5	44.2 (5)
O1A—C1—C2—N2	170.9 (5)	C1—O5—C5—C6	−176.3 (3)
O5—C1—C2—N2	−67.0 (4)	C1—O5—C5—C4	62.9 (4)
O1—C1—C2—C3	172.4 (4)	O4—C4—C5—O5	−169.3 (3)
O1A—C1—C2—C3	−67.0 (5)	C3—C4—C5—O5	−50.4 (4)
O5—C1—C2—C3	55.1 (5)	O4—C4—C5—C6	73.5 (4)
N2—C2—C3—O3	−48.8 (4)	C3—C4—C5—C6	−167.6 (3)
C1—C2—C3—O3	−169.4 (3)	O5—C5—C6—O6	70.9 (4)
N2—C2—C3—C4	74.6 (4)	C4—C5—C6—O6	−169.5 (3)
C1—C2—C3—C4	−46.1 (5)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O \cdots Cl1 ⁱ	0.78 (8)	2.38 (8)	3.151 (3)	173 (7)
O6—H6O \cdots Cl1 ⁱⁱ	0.81 (6)	2.33 (6)	3.123 (3)	171 (6)
O1a—H1Oa \cdots O3 ⁱⁱⁱ	0.94 (17)	1.88 (17)	2.785 (6)	160 (14)
O1A—H1OA \cdots Cl1 ^{iv}	0.90 (18)	2.70 (18)	3.247 (9)	120 (12)
O1A—H1OA \cdots O4 ^{iv}	0.90 (18)	2.15 (17)	3.017 (10)	160 (15)
O4—H4O \cdots Cl1	0.79 (6)	2.29 (6)	3.077 (3)	172 (6)
N2—H2NB \cdots O6 ^v	0.84 (4)	1.92 (4)	2.762 (4)	172 (4)
N2—H2NC \cdots O4 ^{vi}	0.90 (6)	2.11 (6)	2.960 (5)	157 (5)
N2—H2NA \cdots Cl1 ^{vii}	0.98 (6)	2.27 (6)	3.179 (4)	153 (4)

Symmetry codes: (i) $-x+1, y-1/2, -z+3/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $-x+1, y+1/2, -z+1/2$; (iv) $-x+1/2, -y+1, z-1/2$; (v) $-x+1, y-1/2, -z+1/2$; (vi) $x+1/2, -y+1/2, -z+1$; (vii) $-x+3/2, -y+1, z-1/2$.