

Pyridin-1-ium carboxyformate–2-chloroacetic acid (1/1)

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Received 26 November 2024

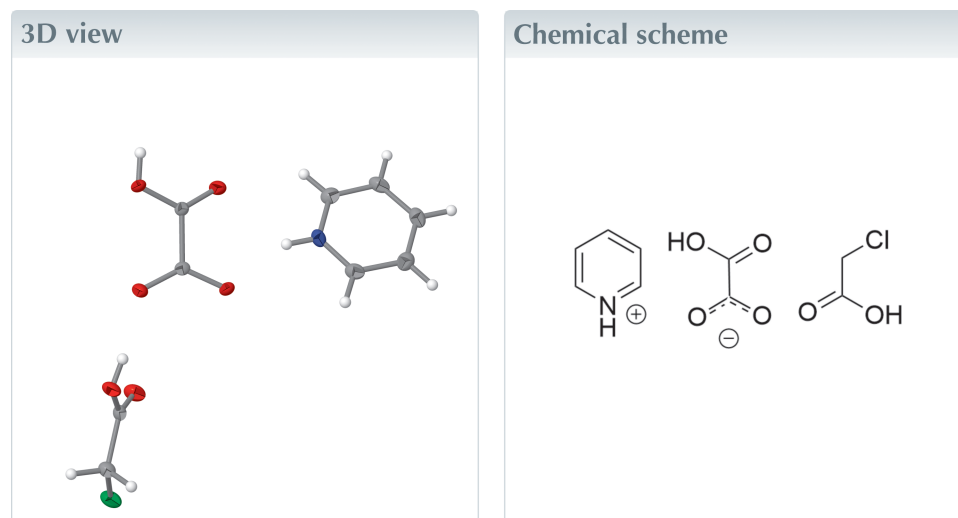
Accepted 24 December 2024

Keywords: crystal structure; co-crystal; salt; non-covalent interactions; hydrogen-bonding.

CCDC reference: 2412697

Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title salt co-crystal, $C_5H_6N^+ \cdot C_2HO_4^- \cdot C_2H_3ClO_2$, comprises a pyridinium cation, a carboxyformate anion and a 2-chloroacetic acid molecule. In the crystal, the components are connected by hydrogen bonds within a one-dimensional chain in the *a*-axis direction which incorporates rather short, charge-assisted O–H...O hydrogen bonds; the pyridinium-NH group forms bifurcated N–H...O(O) hydrogen bonds of different strength.



Structure description

Crystal engineering of co-crystals has inspired great interest from researchers in recent times due to their ability to improve functional properties of materials including pharmaceutical active ingredients (Braga *et al.*, 2013). The selection of synthons or tectons is an important synthetic step to improve the performance of co-crystals, such as solubility, catalytic activity, dissolution profile, pharmacokinetics and stability (Jlassi *et al.*, 2014; Mahmoudi *et al.*, 2017*a,b*). Designing weak intra- or intermolecular interactions and the procedures underlying synthesis constitute the operational part of the crystal engineering endeavour (Abdelhamid *et al.*, 2011; Afkhami *et al.*, 2017). The use of various types of non-covalent interactions in the design of multi-component co-crystals is based on a complete knowledge of these weak bonds, especially supramolecular synthons (Berry *et al.*, 2017; Gurbanov *et al.*, 2018, 2020; Kopylovich *et al.*, 2012*a,b*).

The asymmetric unit of the title compound is shown in Fig. 1. The pyridinium cation, the carboxyformate anion and the chloroacetic acid molecule interact through hydrogen bonds as described below. The C–OH bond lengths for the chloroacetic- and oxalate-

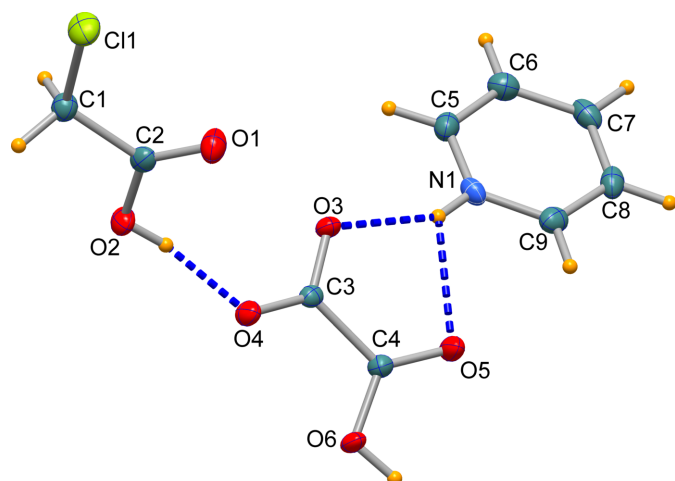


Figure 1
Molecular structures of the components of the asymmetric unit, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

bound carboxylate groups, of 1.3215 (19) and 1.3073 (17) Å, respectively, are longer in comparison to the C=O bond lengths, which range from 1.2074 (19) Å (chloroacetic acid) to 1.2653 (17) Å. These observations clearly confirm the positions of the H atoms, which were located in difference-Fourier maps and refined. The C1–C1 bond length is 1.7755 (15) Å with this bond being in an eclipsed conformation as the C11–C1–C2–O1 torsion angle is $-6.4(2)^\circ$. This torsion angle results in a molecular conformation that is close to planar (C_s symmetry) and corresponds to the ground state of the molecule, as confirmed by quantum chemical calculations (Ananyev *et al.*, 2014).

In the crystal, the species are connected by hydrogen bonds within a linear one-dimensional chain extending along the *a*-axis direction (Fig. 2); a space-filling representation is displayed in Fig. 3. The O–H···O hydrogen bonds, Table 1, are rather short with O···O separations of 2.5834 (14) and 2.6209 (15) Å, while the pyridinium-NH group forms bifurcated N–H···(O,O) hydrogen bonds of different strength, with N···O distances of 2.7935 (16) and 2.9546 (17) Å. These ribbons interact through non-conventional C–H···O hydrogen bonds that consolidate the supramolecular network, Table 1. Within the chain, the pyridinium mean plane forms a

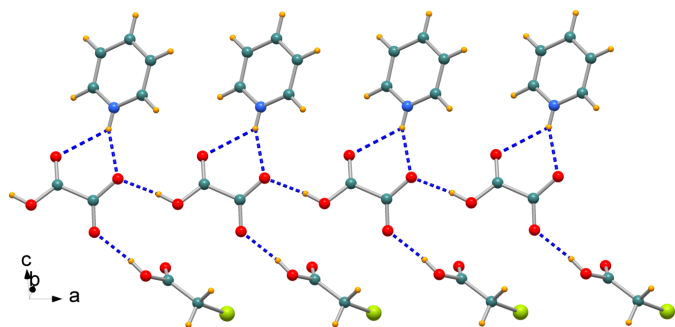


Figure 2
A view of the one-dimensional chain along the *a*-axis direction and featuring hydrogen bonds shown as blue dashed lines.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2–H2 ^o ···O4	0.82 (2)	1.81 (2)	2.6209 (15)	170 (2)
O6–H6 ^o ···O3 ⁱ	0.86 (2)	1.72 (2)	2.5834 (14)	171.8 (19)
N1–H1 ⁿ ···O3	0.861 (19)	1.995 (19)	2.7935 (16)	153.8 (17)
N1–H1 ⁿ ···O5	0.861 (19)	2.339 (18)	2.9546 (17)	128.7 (15)
C1–H1 ^a ···O1 ⁱⁱ	0.99	2.54	3.4555 (19)	153
C1–H1 ^b ···O4 ⁱⁱⁱ	0.99	2.56	3.3439 (19)	136
C5–H5···O6 ^{iv}	0.95	2.59	3.3946 (18)	142
C8–H8···O1 ^v	0.95	2.40	3.3400 (19)	172
C9–H9···O5	0.95	2.49	3.0356 (19)	116

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

dihedral angle of $25.92(6)^\circ$ with the adjacent carboxylate anion, which in turn is twisted by $63.73(4)^\circ$ with respect to the mean plane through the chloroacetic acid molecule.

Chloroacetic acid is a strong carboxylic acid with $pK_a = 2.7$ (Kartrum *et al.*, 1961). A search of the Cambridge Structural Database (CSD: version 5.45, March 2024; Groom *et al.*, 2016) retrieved 39 hits containing chloroacetic acid. Two polymorphs are known, *i.e.* the α - (Kanters & Roelofsen, 1976) and β -forms (Kanters *et al.*, 1976). The α -form has two molecules in the asymmetric unit and has been subjected to a variable temperature study, *i.e.* in the range from 90 to 210 K (Ananyev *et al.*, 2014). This study shows the Cl–C–C=O torsion angles average $22.33(5)$ and $1.30(5)^\circ$ in the two independent molecules over the temperature range (Ananyev *et al.*, 2014). Štoček *et al.* (2022) analysed the position of the H atom in the O–H···N hydrogen bond of the structure of chloroacetic acid with pyridine-4-carboxamide at ten different temperatures. It is also worth noting the crystal structure of quinolinium 2-carboxylate with 2-chloroacetic acid, a species known to exhibit anti-diabetic activity (Kavitha *et al.*, 2021).

Synthesis and crystallization

A mixture of oxalic acid (0.1 mmol), 2-chloroacetic acid (0.1 mmol) and pyridine (0.1 mmol) in methanol (15 ml) was kept for crystallization. The title compound was obtained as a colourless crystals after 2–3 days, yield 87%.

Analysis calculated for $C_9H_{10}ClNO_6$ ($M = 263.63$): C 41.00, H 3.82, N 5.31; Found: C 40.89, H 3.77, N 5.29%. 1H NMR

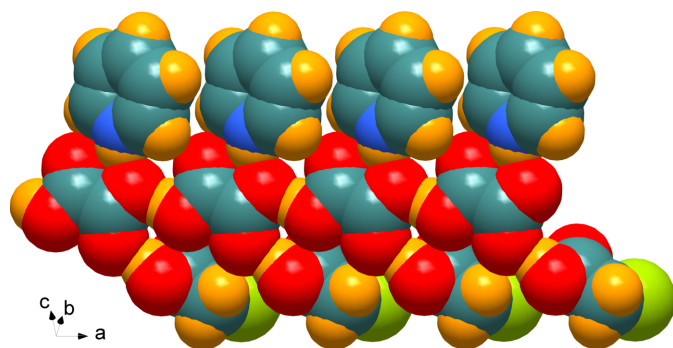


Figure 3
Space-filling representation of the one-dimensional chain.

(300 MHz, DMSO) δ 10.50 (1H, NH), 7.45–8.62 (5H, py) and 4.27 (2H, CH₂); OH not observed. ¹³C NMR (75 MHz, DMSO) δ 41.59, 124.44, 137.53, 148.70, 161.49, 168.72 and 169.23. ESI-MS: *m/z*: 264.58 [*M*+H]⁺.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms of the carboxylate and pyridinium ions were refined freely.

Acknowledgements

This work was supported by Baku State University (Azerbaijan), Western Caspian University (Azerbaijan), Azerbaijan Medical University, Baku Engineering University (Azerbaijan) and Khazar University (Azerbaijan).

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₅ H ₆ N ⁺ ·C ₂ H ₄ O ₄ ⁻ ·C ₂ H ₃ ClO ₂
<i>M_r</i>	263.63
Crystal system, space group	Monoclinic, <i>P</i> ₂ /c
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.6911 (4), 7.9862 (4), 24.9303 (14)
β (°)	91.008 (3)
<i>V</i> (Å ³)	1132.91 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.35
Crystal size (mm)	0.37 × 0.26 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.872, 0.939
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7091, 2127, 1963
<i>R</i> _{int}	0.030
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.611
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.082, 1.10
No. of reflections	2127
No. of parameters	163
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.19, -0.32

Computer programs: *APEX4* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *DIAMOND* (Brandenburg, 1999).

full crystallographic data

IUCrData (2025). **10**, x241242 [<https://doi.org/10.1107/S2414314624012422>]

Pyridin-1-ium carboxyformate–2-chloroacetic acid (1/1)

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Pyridin-1-ium carboxyformate–2-chloroacetic acid (1/1)

Crystal data

$C_5H_6N^+ \cdot C_2HO_4^- \cdot C_2H_3ClO_2$

$M_r = 263.63$

Monoclinic, $P2_1/c$

$a = 5.6911$ (4) Å

$b = 7.9862$ (4) Å

$c = 24.9303$ (14) Å

$\beta = 91.008$ (3)°

$V = 1132.91$ (12) Å³

$Z = 4$

$F(000) = 544$

$D_x = 1.546$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4685 reflections

$\theta = 2.7$ – 25.7°

$\mu = 0.35$ mm⁻¹

$T = 150$ K

Plate, colourless

$0.37 \times 0.26 \times 0.15$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.872$, $T_{\max} = 0.939$

7091 measured reflections

2127 independent reflections

1963 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 25.7^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -4 \rightarrow 6$

$k = -9 \rightarrow 9$

$l = -30 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.082$

$S = 1.10$

2127 reflections

163 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 0.480P]$

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

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

$\Delta\rho_{\max} = 0.19$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ e Å⁻³

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.30381 (7)	0.60040 (5)	0.25074 (2)	0.02973 (14)
O1	0.8928 (2)	0.68016 (13)	0.31709 (5)	0.0274 (3)
O2	0.8175 (2)	0.41486 (13)	0.34182 (4)	0.0219 (3)
H2o	0.717 (4)	0.457 (2)	0.3605 (8)	0.033*
O3	0.62947 (17)	0.65703 (12)	0.47108 (4)	0.0177 (2)
O4	0.47024 (18)	0.51382 (13)	0.40178 (4)	0.0202 (2)
O5	0.19134 (18)	0.77629 (14)	0.49141 (5)	0.0259 (3)
O6	0.04269 (18)	0.56931 (13)	0.44029 (4)	0.0193 (2)
H6o	−0.090 (4)	0.608 (2)	0.4516 (8)	0.029*
N1	0.5976 (2)	0.86111 (15)	0.56167 (5)	0.0196 (3)
H1n	0.561 (3)	0.807 (2)	0.5329 (8)	0.024*
C1	1.1476 (3)	0.45380 (19)	0.29004 (6)	0.0211 (3)
H1a	1.091788	0.361048	0.266754	0.025*
H1b	1.255256	0.405946	0.317640	0.025*
C2	0.9388 (3)	0.53258 (18)	0.31738 (6)	0.0183 (3)
C3	0.4606 (2)	0.60253 (16)	0.44239 (6)	0.0146 (3)
C4	0.2140 (2)	0.65877 (17)	0.46095 (5)	0.0152 (3)
C5	0.8036 (3)	0.83223 (19)	0.58675 (6)	0.0222 (3)
H5	0.908910	0.750929	0.573162	0.027*
C6	0.8617 (3)	0.92126 (19)	0.63237 (6)	0.0244 (3)
H6	1.007643	0.902500	0.650458	0.029*
C7	0.7051 (3)	1.03825 (19)	0.65155 (6)	0.0245 (4)
H7	0.743544	1.100904	0.682892	0.029*
C8	0.4919 (3)	1.06414 (18)	0.62502 (6)	0.0236 (3)
H8	0.382242	1.143181	0.638176	0.028*
C9	0.4420 (3)	0.97347 (18)	0.57938 (6)	0.0221 (3)
H9	0.297675	0.990351	0.560428	0.027*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0322 (3)	0.0305 (2)	0.0269 (2)	−0.00243 (17)	0.01274 (18)	−0.00068 (16)
O1	0.0301 (6)	0.0210 (6)	0.0315 (6)	0.0058 (5)	0.0080 (5)	−0.0001 (5)
O2	0.0218 (6)	0.0212 (5)	0.0230 (6)	0.0007 (4)	0.0081 (5)	−0.0047 (4)
O3	0.0113 (5)	0.0204 (5)	0.0212 (5)	0.0000 (4)	−0.0005 (4)	−0.0032 (4)
O4	0.0167 (5)	0.0245 (5)	0.0197 (5)	−0.0009 (4)	0.0043 (4)	−0.0068 (4)
O5	0.0165 (6)	0.0284 (6)	0.0329 (6)	−0.0011 (5)	0.0039 (5)	−0.0153 (5)
O6	0.0100 (5)	0.0251 (5)	0.0229 (6)	−0.0001 (4)	0.0002 (4)	−0.0077 (4)
N1	0.0252 (7)	0.0165 (6)	0.0173 (6)	−0.0043 (5)	0.0025 (5)	−0.0038 (5)
C1	0.0218 (8)	0.0212 (7)	0.0203 (7)	0.0014 (6)	0.0034 (6)	−0.0013 (6)
C2	0.0179 (7)	0.0218 (7)	0.0150 (7)	0.0001 (6)	−0.0013 (6)	−0.0032 (6)
C3	0.0138 (7)	0.0139 (6)	0.0160 (7)	−0.0003 (5)	0.0015 (6)	0.0025 (5)
C4	0.0138 (7)	0.0177 (7)	0.0140 (7)	−0.0004 (5)	0.0002 (5)	0.0008 (5)
C5	0.0220 (8)	0.0182 (7)	0.0265 (8)	0.0016 (6)	0.0055 (6)	−0.0003 (6)
C6	0.0230 (8)	0.0250 (8)	0.0251 (8)	−0.0032 (6)	−0.0014 (7)	0.0009 (6)

C7	0.0336 (9)	0.0203 (7)	0.0198 (8)	-0.0076 (7)	0.0045 (7)	-0.0035 (6)
C8	0.0288 (9)	0.0158 (7)	0.0264 (8)	0.0018 (6)	0.0107 (7)	0.0000 (6)
C9	0.0200 (8)	0.0194 (7)	0.0271 (8)	-0.0009 (6)	0.0011 (6)	0.0035 (6)

Geometric parameters (Å, °)

C11—C1	1.7755 (15)	C1—H1a	0.9900
O1—C2	1.2074 (19)	C1—H1b	0.9900
O2—C2	1.3215 (19)	C3—C4	1.551 (2)
O2—H2o	0.82 (2)	C5—C6	1.377 (2)
O3—C3	1.2653 (17)	C5—H5	0.9500
O4—C3	1.2377 (17)	C6—C7	1.382 (2)
O5—C4	1.2155 (18)	C6—H6	0.9500
O6—C4	1.3073 (17)	C7—C8	1.388 (2)
O6—H6o	0.86 (2)	C7—H7	0.9500
N1—C5	1.339 (2)	C8—C9	1.374 (2)
N1—C9	1.341 (2)	C8—H8	0.9500
N1—H1n	0.861 (19)	C9—H9	0.9500
C1—C2	1.517 (2)		
C2—O2—H2o	110.2 (14)	O5—C4—C3	121.09 (13)
C4—O6—H6o	109.1 (13)	O6—C4—C3	113.36 (12)
C5—N1—C9	122.63 (14)	N1—C5—C6	119.49 (14)
C5—N1—H1n	120.0 (12)	N1—C5—H5	120.3
C9—N1—H1n	117.3 (12)	C6—C5—H5	120.3
C2—C1—C11	112.23 (10)	C5—C6—C7	119.22 (15)
C2—C1—H1a	109.2	C5—C6—H6	120.4
C11—C1—H1a	109.2	C7—C6—H6	120.4
C2—C1—H1b	109.2	C6—C7—C8	119.97 (14)
C11—C1—H1b	109.2	C6—C7—H7	120.0
H1a—C1—H1b	107.9	C8—C7—H7	120.0
O1—C2—O2	125.61 (14)	C9—C8—C7	118.84 (14)
O1—C2—C1	125.02 (14)	C9—C8—H8	120.6
O2—C2—C1	109.37 (12)	C7—C8—H8	120.6
O4—C3—O3	127.95 (13)	N1—C9—C8	119.83 (15)
O4—C3—C4	117.59 (12)	N1—C9—H9	120.1
O3—C3—C4	114.44 (12)	C8—C9—H9	120.1
O5—C4—O6	125.55 (13)		
C11—C1—C2—O1	-6.4 (2)	C9—N1—C5—C6	-0.5 (2)
C11—C1—C2—O2	174.23 (10)	N1—C5—C6—C7	0.4 (2)
O4—C3—C4—O5	-161.69 (14)	C5—C6—C7—C8	0.3 (2)
O3—C3—C4—O5	17.27 (19)	C6—C7—C8—C9	-0.9 (2)
O4—C3—C4—O6	17.70 (18)	C5—N1—C9—C8	0.0 (2)
O3—C3—C4—O6	-163.35 (12)	C7—C8—C9—N1	0.7 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 o \cdots O4	0.82 (2)	1.81 (2)	2.6209 (15)	170 (2)
O6—H6 o \cdots O3 ⁱ	0.86 (2)	1.72 (2)	2.5834 (14)	171.8 (19)
N1—H1 n \cdots O3	0.861 (19)	1.995 (19)	2.7935 (16)	153.8 (17)
N1—H1 n \cdots O5	0.861 (19)	2.339 (18)	2.9546 (17)	128.7 (15)
C1—H1 a \cdots O1 ⁱⁱ	0.99	2.54	3.4555 (19)	153
C1—H1 b \cdots O4 ⁱⁱⁱ	0.99	2.56	3.3439 (19)	136
C5—H5 \cdots O6 ^{iv}	0.95	2.59	3.3946 (18)	142
C8—H8 \cdots O1 ^v	0.95	2.40	3.3400 (19)	172
C9—H9 \cdots O5	0.95	2.49	3.0356 (19)	116

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