Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

N-(2-Carboxyethyl)-2,5-dideoxy-2,5-imino-D-mannonic acid [(3*R*,4*R*,5*R*)-1-(2-carboxyethyl)-3,4-dihydroxy-5-hydroxymethyl-L-proline]

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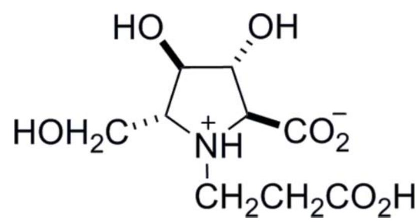
Received 24 August 2012; accepted 30 August 2012

Key indicators: single-crystal X-ray study; *T* = 190 K; mean σ(C–C) = 0.002 Å; *R* factor = 0.024; *wR* factor = 0.062; data-to-parameter ratio = 8.9.

The absolute stereochemistry of the title compound, $C_9H_{15}NO_7$, was determined from the use of D-glucuronolactone as the starting material. The compound crystallizes as the zwitterion. The five-membered ring adopts an envelope conformation with the –CH_2OH-substituted C atom forming the flap. An intramolecular N—H···O hydrogen-bond occurs. In the crystal, the compound exists as a three-dimensional O—H···O intermolecular hydrogen-bonded network with each molecule acting as a donor and acceptor for four hydrogen bonds.

Related literature

For related literature on naturally occurring iminosugars, see: Asano *et al.* (2000); Watson *et al.* (2001); Nash *et al.* (1991); Welter *et al.* (1976); Manning *et al.* (1985); Pereira *et al.* (1991). For the synthesis of the diacid, see: Best *et al.* (2010); Martínez *et al.* (2012). For the extinction correction, see: Larson (1970). For hydrogen-atom refinement, see: Cooper *et al.* (2010). For the temperature controller, see: Cosier & Glazer (1986). For the Chebychev polynomial used in the weighting scheme, see: Prince (1982); Watkin (1994).



Experimental

Crystal data

$C_9H_{15}NO_7$
M_r = 249.22
Orthorhombic, $P2_12_12_1$
a = 8.5242 (1) Å
b = 8.5707 (1) Å
c = 14.3585 (3) Å
V = 1049.01 (3) Å^3
Z = 4
Mo *Kα* radiation
μ = 0.14 mm^{-1}
T = 190 K
0.32 × 0.30 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.93, T_{max} = 0.99
18435 measured reflections
1385 independent reflections
1321 reflections with $I > 2\sigma(I)$
R_{int} = 0.009

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.062
S = 0.93
1385 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O17—H171···O15^{i}	0.84	2.19	2.887 (2)	141
O14—H141···O10^{ii}	0.86	1.78	2.618 (2)	166
O1—H11···O10^{iii}	0.82	1.95	2.753 (2)	165
O4—H41···O9^{i}	0.82	1.93	2.720 (2)	163
N6—H61···O15	0.90	2.15	2.768 (2)	125

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (iii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *Superflip* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

This work was supported by the Fundación Ramón Areces (RFM).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5524).

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supporting information

Acta Cryst. (2012). E**68**, o2865–o2866 [https://doi.org/10.1107/S1600536812037488]

N-(2-Carboxyethyl)-2,5-dideoxy-2,5-imino-D-mannonic acid [(3*R*,4*R*,5*R*)-1-(2-carboxyethyl)-3,4-dihydroxy-5-hydroxymethyl-L-proline]

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S1. Comment

More than 250 iminosugars, sugar mimics in which the ring oxygen in a pyranose or furanose is replaced by nitrogen to form polyhydroxylated piperidines and pyrrolidines, have been isolated from plants (Asano *et al.*, 2000; Watson *et al.*, 2001). DMDP **1** (Fig. 1), originally isolated from *Derris eliptica* (Welter *et al.*, 1976), but the most widely occurring iminosugar, is even found in potatoes (Nash *et al.*, 1991). In contrast, BR1 **2** from *Baphia racemosa* (Manning *et al.*, 1985) and 7a-epialexaflorine **3** from *Alexa grandiflora* (Pereira *et al.*, 1991) are among the very few corresponding sugar amino acids (SAA) found in nature. From examination of crude extracts of plants, it is clear that other SAA are natural products. As part of a program to make authentic samples of such SAA to identify them in crude plant extracts, the SAA corresponding to DMDP **4** (Best *et al.*, 2010) was converted to the diacid **5** by initial reaction with *tert*-butyl acrylate in methanol in the presence of triethylamine followed by treatment with aqueous trifluoroacetic acid (Martínez, 2012). The structure of **5** was unequivocally determined by X-ray crystallographic analysis; the absolute configuration was determined by the use of *d*-glucuronolactone as the starting material for the synthesis.

The five ring adopts an envelope conformation with C5 out of the plane (Fig. 2). The compound exisits as a three-dimensional O—H···O intermolecular hydrogen-bonded network with each molecule acting as a donor and acceptor for four hydrogen bonds (Fig. 3).

S2. Experimental

The synthetic procedure is described in the comment section and illustrated in Fig. 1. The title compound was recrystallized from water: $[\alpha]_D^{25}$ -6.7 (*c* 0.75 in H_2O); m.p. 523 K (decomposed).

S3. Refinement

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the starting material.

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, O—H = 0.82 Å) and *U*iso~(H) (in the range 1.2–1.5 times *U*~eq~ of the parent atom), after which the positions were refined with riding constraints (Cooper *et al.*, 2010).

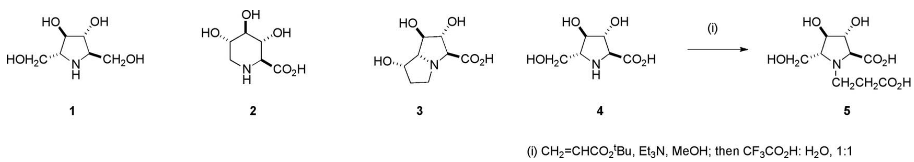

Figure 1

Synthetic Scheme.

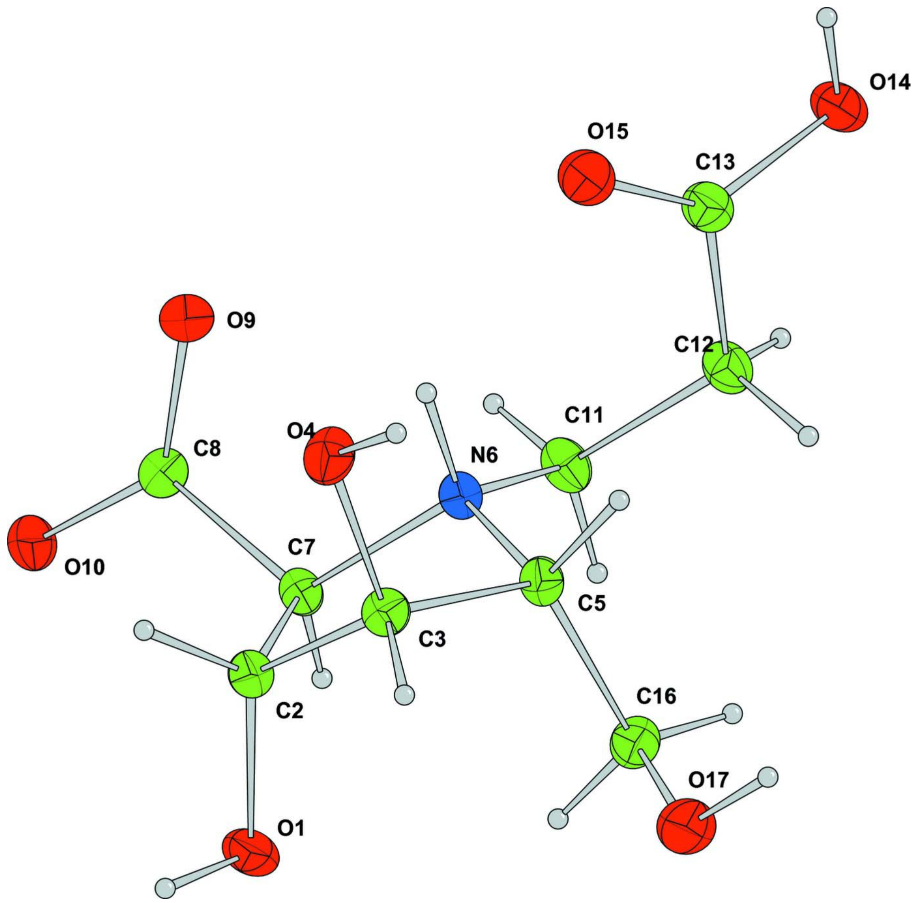

Figure 2

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

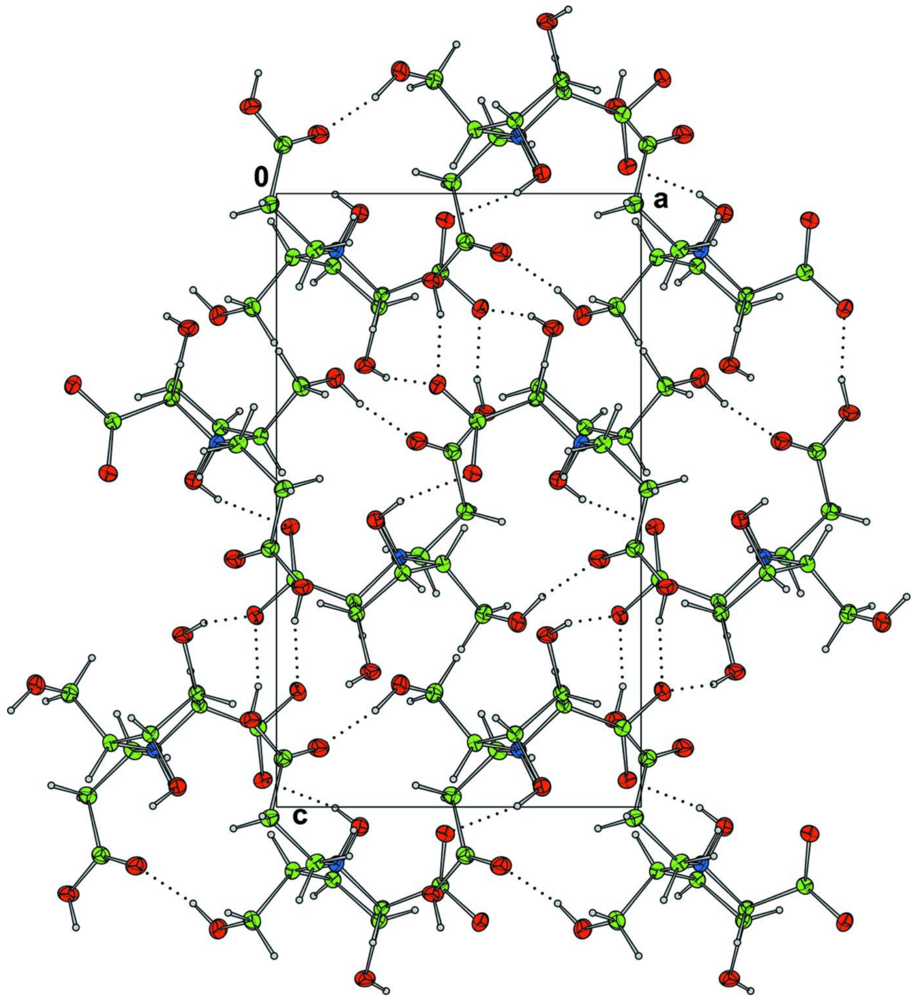

Figure 3

Packing diagram of the title compound projected along the *b*-axis. Hydrogen bonds are shown as dotted lines.

N-(2-Carboxyethyl)-2,5-dideoxy-2,5-imino-*D*-mannonic acid

Crystal data

$C_9H_{15}NO_7$
$M_r = 249.22$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 8.5242$ (1) Å
$b = 8.5707$ (1) Å
$c = 14.3585$ (3) Å
$V = 1049.01$ (3) Å^3
$Z = 4$
$F(000) = 528$
$D_x = 1.578$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1401 reflections
$\theta = 5$–27°
$\mu = 0.14$ mm^{-1}
$T = 190$ K
Plate, colourless
0.32 × 0.30 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.93$, $T_{max} = 0.99$

18435 measured reflections
1385 independent reflections
1321 reflections with $I > 2\sigma(I)$
$R_{int} = 0.009$

$\theta_{max} = 27.5°$, $\theta_{min} = 5.3°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 0.93$
1385 reflections
155 parameters
0 restraints
Primary atom site location: Other
Hydrogen site location: difference Fourier map
H-atom parameters constrained

Method, part 1, Chebychev polynomial, (Watkin, 1994; *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below *w* and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 24.6 39.9 23.9 10.2 2.48
$(\Delta/\sigma)_{max} = 0.0004353$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 190 (20)

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat (Cosier & Glazer, 1986) with a nominal stability of 0.1 K.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.25779 (14)	0.79237 (13)	0.78008 (7)	0.0203
C2	0.21884 (17)	0.76687 (17)	0.68515 (10)	0.0156
C3	0.34616 (17)	0.82784 (16)	0.61866 (10)	0.0153
O4	0.27181 (12)	0.86546 (13)	0.53261 (7)	0.0199
C5	0.45582 (16)	0.68918 (15)	0.60409 (9)	0.0148
N6	0.33646 (14)	0.56002 (13)	0.59290 (8)	0.0141
C7	0.21204 (16)	0.58889 (17)	0.66539 (10)	0.0144
C8	0.05081 (18)	0.54093 (16)	0.62872 (10)	0.0155
O9	0.03760 (13)	0.51412 (12)	0.54371 (7)	0.0196
O10	−0.05866 (13)	0.53953 (13)	0.68791 (7)	0.0205
C11	0.39382 (17)	0.39407 (16)	0.59147 (11)	0.0168
C12	0.51896 (18)	0.36273 (17)	0.51838 (9)	0.0177
C13	0.48212 (17)	0.41891 (17)	0.42111 (10)	0.0178
O14	0.57147 (14)	0.35134 (13)	0.35801 (7)	0.0218
O15	0.38504 (14)	0.51908 (13)	0.40387 (7)	0.0241
C16	0.56756 (17)	0.66168 (17)	0.68540 (11)	0.0191
O17	0.66018 (13)	0.79709 (15)	0.69892 (8)	0.0252
H21	0.1206	0.8129	0.6680	0.0190*
H31	0.3983	0.9179	0.6450	0.0177*
H51	0.5150	0.6992	0.5452	0.0178*
H71	0.2358	0.5326	0.7211	0.0155*
H111	0.3007	0.3304	0.5802	0.0199*
H112	0.4377	0.3698	0.6517	0.0210*

H121	0.5390	0.2510	0.5152	0.0211*
H122	0.6181	0.4132	0.5352	0.0221*
H162	0.6327	0.5676	0.6725	0.0238*
H161	0.5065	0.6450	0.7429	0.0230*
H171	0.7288	0.8063	0.6573	0.0384*
H141	0.5503	0.3854	0.3035	0.0342*
H11	0.1995	0.8611	0.8000	0.0308*
H41	0.3391	0.9087	0.5016	0.0308*
H61	0.2882	0.5748	0.5379	0.0220*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0242 (5)	0.0209 (5)	0.0158 (5)	0.0028 (5)	0.0009 (4)	−0.0050 (4)
C2	0.0150 (6)	0.0164 (6)	0.0153 (6)	0.0016 (5)	0.0004 (5)	−0.0010 (5)
C3	0.0158 (6)	0.0143 (6)	0.0158 (6)	0.0003 (5)	−0.0004 (5)	0.0005 (5)
O4	0.0173 (5)	0.0230 (5)	0.0195 (5)	0.0015 (4)	0.0003 (4)	0.0065 (4)
C5	0.0133 (6)	0.0146 (6)	0.0166 (6)	−0.0001 (5)	0.0012 (5)	−0.0005 (5)
N6	0.0134 (5)	0.0142 (5)	0.0148 (5)	0.0008 (4)	0.0011 (5)	−0.0004 (4)
C7	0.0144 (6)	0.0148 (6)	0.0140 (6)	0.0014 (5)	0.0020 (5)	0.0002 (5)
C8	0.0161 (6)	0.0137 (6)	0.0167 (6)	−0.0004 (5)	−0.0008 (5)	0.0016 (5)
O9	0.0196 (5)	0.0233 (5)	0.0160 (5)	0.0003 (5)	−0.0016 (4)	−0.0015 (4)
O10	0.0154 (5)	0.0266 (5)	0.0196 (5)	−0.0028 (4)	0.0036 (4)	−0.0011 (4)
C11	0.0202 (7)	0.0124 (6)	0.0179 (6)	0.0024 (5)	0.0038 (6)	0.0012 (5)
C12	0.0198 (7)	0.0157 (6)	0.0176 (6)	0.0034 (6)	0.0020 (6)	−0.0005 (5)
C13	0.0184 (6)	0.0176 (6)	0.0174 (6)	−0.0005 (6)	0.0013 (6)	−0.0020 (5)
O14	0.0257 (6)	0.0246 (5)	0.0151 (5)	0.0056 (5)	0.0016 (4)	−0.0016 (4)
O15	0.0254 (5)	0.0277 (6)	0.0191 (5)	0.0085 (5)	−0.0010 (5)	0.0005 (4)
C16	0.0168 (6)	0.0195 (7)	0.0209 (7)	0.0018 (6)	−0.0022 (6)	−0.0029 (6)
O17	0.0189 (5)	0.0334 (6)	0.0232 (5)	−0.0089 (5)	0.0013 (5)	−0.0051 (5)

Geometric parameters (Å, º)

O1—C2	1.4198 (17)	C7—H71	0.956
O1—H11	0.822	C8—O9	1.2471 (17)
C2—C3	1.537 (2)	C8—O10	1.2622 (18)
C2—C7	1.553 (2)	C11—C12	1.5204 (19)
C2—H21	0.958	C11—H111	0.976
C3—O4	1.4257 (16)	C11—H112	0.965
C3—C5	1.5263 (19)	C12—C13	1.5103 (19)
C3—H31	0.968	C12—H121	0.974
O4—H41	0.815	C12—H122	0.980
C5—N6	1.5121 (17)	C13—O14	1.3177 (18)
C5—C16	1.525 (2)	C13—O15	1.2178 (19)
C5—H51	0.989	O14—H141	0.855
N6—C7	1.5064 (17)	C16—O17	1.4171 (18)
N6—C11	1.5041 (17)	C16—H162	0.997
N6—H61	0.900	C16—H161	0.987

C7—C8	1.528 (2)	O17—H171	0.840

C2—O1—H11	107.6	C2—C7—H71	109.5
O1—C2—C3	112.26 (12)	N6—C7—H71	110.3
O1—C2—C7	109.60 (12)	C8—C7—H71	110.1
C3—C2—C7	104.29 (11)	C7—C8—O9	117.91 (13)
O1—C2—H21	112.8	C7—C8—O10	115.82 (12)
C3—C2—H21	108.5	O9—C8—O10	126.19 (15)
C7—C2—H21	109.0	N6—C11—C12	113.87 (12)
C2—C3—O4	107.53 (11)	N6—C11—H111	105.5
C2—C3—C5	104.65 (11)	C12—C11—H111	110.9
O4—C3—C5	109.24 (11)	N6—C11—H112	108.5
C2—C3—H31	110.6	C12—C11—H112	108.0
O4—C3—H31	111.2	H111—C11—H112	110.1
C5—C3—H31	113.2	C11—C12—C13	115.85 (12)
C3—O4—H41	105.3	C11—C12—H121	109.2
C3—C5—N6	99.93 (10)	C13—C12—H121	107.9
C3—C5—C16	113.45 (11)	C11—C12—H122	111.0
N6—C5—C16	112.86 (11)	C13—C12—H122	105.4
C3—C5—H51	111.2	H121—C12—H122	107.1
N6—C5—H51	108.4	C12—C13—O14	112.05 (12)
C16—C5—H51	110.5	C12—C13—O15	123.65 (13)
C5—N6—C7	106.26 (10)	O14—C13—O15	124.25 (14)
C5—N6—C11	118.36 (11)	C13—O14—H141	111.0
C7—N6—C11	113.18 (11)	C5—C16—O17	109.05 (12)
C5—N6—H61	107.3	C5—C16—H162	109.3
C7—N6—H61	105.2	O17—C16—H162	112.2
C11—N6—H61	105.7	C5—C16—H161	109.5
C2—C7—N6	105.15 (11)	O17—C16—H161	107.4
C2—C7—C8	111.15 (12)	H162—C16—H161	109.4
N6—C7—C8	110.54 (11)	C16—O17—H171	111.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H51···O4^{i}	0.99	2.52	3.366 (2)	143 (1)
C7—H71···O17^{ii}	0.96	2.49	3.352 (2)	151 (1)
C11—H112···O17^{ii}	0.97	2.38	3.156 (2)	137 (1)
C12—H121···O9^{iii}	0.97	2.43	3.354 (2)	160 (1)
C12—H122···O4^{i}	0.98	2.50	3.257 (2)	134 (1)
C16—H161···O1	0.99	2.53	3.174 (2)	123
O17—H171···O15^{i}	0.84	2.19	2.887 (2)	141 (1)
O14—H141···O10^{iv}	0.86	1.78	2.618 (2)	166 (1)
O1—H11···O10^{v}	0.82	1.95	2.753 (2)	165 (1)
O4—H41···O9^{i}	0.82	1.93	2.720 (2)	163 (1)
N6—H61···O15	0.90	2.15	2.768 (2)	125

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