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4-Carboxypyridin-1-ium 2,4,5-tricarboxybenzoate monohydrate

Hadi D. Arman^a and Edward R. T. Tiekink^{b*}

^aDepartment of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA, and ^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: edward.tiekink@gmail.com

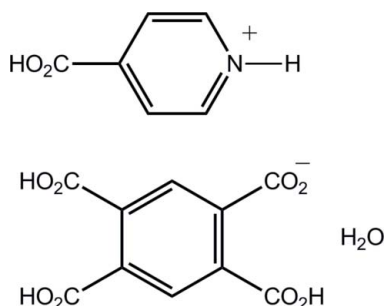
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Key indicators: single-crystal X-ray study; $T = 98$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.056; wR factor = 0.133; data-to-parameter ratio = 12.1.

The title hydrated salt, $\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{H}_2\text{O}$, was isolated from the 1:1 cocrystallization of benzene-1,2,4,5-tetracarboxylic acid and isonicotinic acid in ethanol solution. In the crystal, the cation is close to planar [r.m.s. deviation = 0.085 Å for the nine fitted atoms; the C—C—C—O(carbonyl) torsion angle = -8.7 (4)°], but twists are evident in the anion, with all but the carboxylic acid group diagonally opposite the carboxylate group being significantly twisted out of the plane of the benzene ring [C—C—C—O(carbonyl) torsion angles = -118.1 (2), -157.6 (2), 4.3 (3) and 77.3 (3)°]. In the crystal, the ions and water molecules are consolidated into a three-dimensional architecture by O—H...O and N—H...O hydrogen bonding along with C—H...O interactions.

Related literature

For background to pharmaceutical co-crystals, see: Almarsson & Zaworotko (2004). For related co-crystallization studies on 1,2,4,5-benzenetetracarboxylic acid, see: Arman & Tiekink (2013*a,b*). For the structure of isonicotinic acid, see: Takusagawa & Shimada (1976). For the structure of the analogous salt formed from nicotinic acid, see: Dos Santos *et al.* (2012). For the calculation of pK_a values, see: Chemaxon (2009).



Experimental

Crystal data

$\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{H}_2\text{O}$
 $M_r = 395.27$
 Triclinic, $P\bar{1}$
 $a = 9.724$ (2) Å
 $b = 10.007$ (2) Å
 $c = 10.755$ (2) Å
 $\alpha = 99.56$ (1)°
 $\beta = 114.667$ (8)°

$\gamma = 110.283$ (9)°
 $V = 830.7$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 98$ K
 $0.33 \times 0.25 \times 0.20$ mm

Data collection

Rigaku AFC12/SATURN724 diffractometer
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.807$, $T_{\max} = 1.000$

5233 measured reflections
 3414 independent reflections
 3200 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.133$
 $S = 1.17$
 3414 reflections
 281 parameters
 8 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O4—H4O...O3 ⁱ	0.84 (3)	1.82 (3)	2.654 (3)	176 (3)
O6—H6O...O1 ⁱⁱ	0.85 (5)	1.69 (5)	2.534 (3)	174 (5)
O8—H8O...O1W	0.85 (5)	1.79 (5)	2.634 (3)	171 (6)
O10—H10O...O2 ⁱⁱⁱ	0.85 (4)	1.78 (4)	2.625 (3)	172 (4)
N1—H1N...O5 ^{iv}	0.89 (4)	1.86 (4)	2.711 (3)	160 (4)
O1W—H1W...O2 ^v	0.85 (2)	2.16 (2)	2.957 (3)	156 (3)
O1W—H2W...O2 ⁱⁱⁱ	0.85 (1)	2.05 (2)	2.853 (3)	158 (4)
C6—H6...O7 ^v	0.95	2.40	3.267 (3)	151
C12—H12...O9 ^{vi}	0.95	2.35	3.179 (4)	146
C14—H14...O6 ^{vii}	0.95	2.40	3.300 (4)	159

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

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7093).

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supporting information

Acta Cryst. (2013). E69, o1122–o1123 [https://doi.org/10.1107/S1600536813016437]

4-Carboxypyridin-1-ium 2,4,5-tricarboxybenzoate monohydrate

Hadi D. Arman and Edward R. Tiekink

S1. Comment

Interest in co-crystallization experiments stems largely from potential applications in the pharmaceutical industry (Almarsson & Zaworotko, 2004). The title salt hydrate, (I), was isolated during an investigation of co-crystallization experiments with 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid; LH₄) and various pyridyl derivatives (Arman & Tiekink, 2013*a*; Arman & Tiekink, 2013*b*).

The 1:1 co-crystallization of pyromellitic acid and isonicotinic acid in an ethanol solution afforded a salt hydrate, (I), there being one complete molecule of the 4-carboxypyridin-1-ium cation, the hydroxy(2,4,5-tricarboxyphenyl)methanolate anion and a water molecule in the asymmetric unit. Confirmation of protonation of isonicotinic acid during crystallization is found in the nature of hydrogen bonding involving the pyridinium cation (see below), and the widening of the C13—N1—C14 angle to 123.1 (2)° *cf.* 118.9 (2)° in the structure of isonicotinic acid itself (Takusagawa & Shimada, 1976). Further, the disparity in the C—O bond lengths of the carboxylic acid residue, $\Delta(\text{C—O}) = [(\text{C—O})_{\text{long}} - (\text{C—O})_{\text{short}}] = 0.10 \text{ \AA}$, confirms that isonicotinic acid has been protonated at N1, rather than existing in a zwitterionic form, with equivalent C—O bonds. Complementing this evidence, in the anion, the $\Delta(\text{C—O})$ value for the O1-carboxylate group is 0.01 Å, indicating considerable delocalization of electron density over the CO₂ atoms, compared to values in the range 0.07 to 0.11 Å for the remaining carboxylic acids.

In the cation, the carboxylic acid residue is approximately co-planar with the pyridyl ring to which it is attached as seen in the C12—C11—C16—O9 torsion angle of -8.7 (4)°. Indeed, the entire cation is approximately planar with the r.m.s. deviation = 0.085 Å for the nine fitted atoms. By contrast, anion is non-planar with the carboxylic acid diagonally opposite the carboxylate group being co-planar to the phenyl ring [C—C—C—O(carbonyl) torsion angle = 4.3 (3)°] but the remaining carboxylic acids and carboxylate residues deviate significantly [C—C—C—O(carbonyl) torsion angles = -118.1 (2), -157.6 (2) and 77.3 (3)°].

The three-dimensional crystal structure of (I) is consolidated by O—H···O and N—H···O hydrogen bonding involving all three components of the structure; geometric parameters characterizing these are summarized in Table 1. Two distinct supramolecular aggregation patterns are clearly discerned, with the first of these being a tape along [1 0 0] comprising hydroxy(2,4,5-tricarboxyphenyl)methanolate anions, Fig. 2, which is sustained by centrosymmetric eight-membered {···O=COH}₂ synthons involving the O3-carboxylic acid and orthogonal O6—H···O1 hydrogen bonds. A supramolecular chain containing alternating cations and anions is also found, Fig. 3. This is aligned along [1 0 - 1] and is stabilized by O10—H···O2 and N1—H···O5 hydrogen bonds. The aforementioned are connected into a supramolecular layer in the *ac* plane. As seen in Fig. 4, the centrosymmetrically related water molecules are bridged by carboxylate-O2 atoms to form an eight-membered {···HOH···O}₂ ring. The water-O1_w atom also accepts a hydrogen bond from the O8—H hydroxyl group. Also evident from the image in Fig. 4 is the critical role played by the trifurcated carboxylate-O2 atom in stabilizing the crystal structure. Several of the oxygen atoms not involved in formal hydrogen bonding interactions participate in C—H···O interactions to consolidate the crystal packing, Fig. 5.

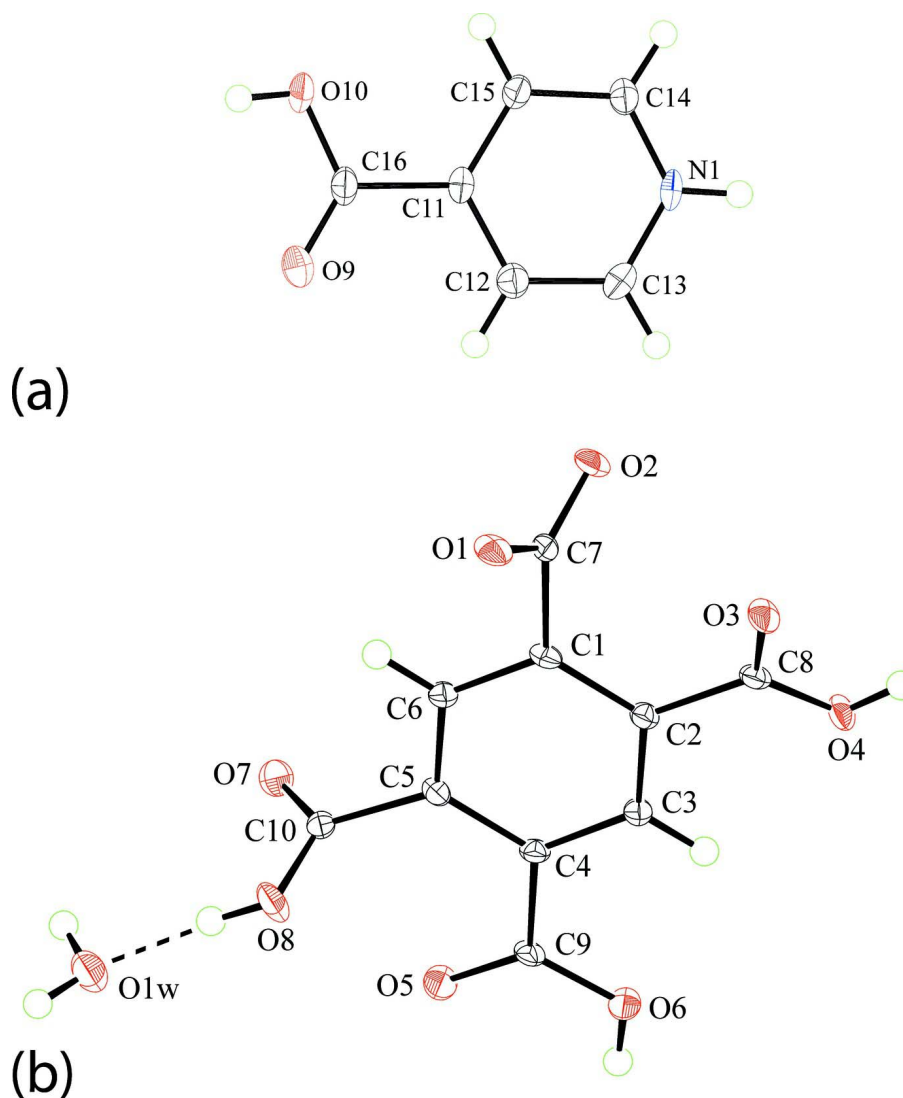
While salt (I) was characterized from the 1:1 co-crystallization of LH_4 with isonicotinic acid in an ethanol solution, the analogous experiment with nicotinic [NA] acid gave a salt of composition $[NAH]_2[LH_2]$ (Dos Santos, *et al.*, 2012). While protonation of NA is not surprising the fact that LH_4 has been doubly deprotonated correlates nicely with the increased basicity of the nitrogen atom in NA *cf.* isonicotinic acid, *i.e.* calculated $pK_a = 4.19$ and 2.35 , respectively (Chemaxon, 2009).

S2. Experimental

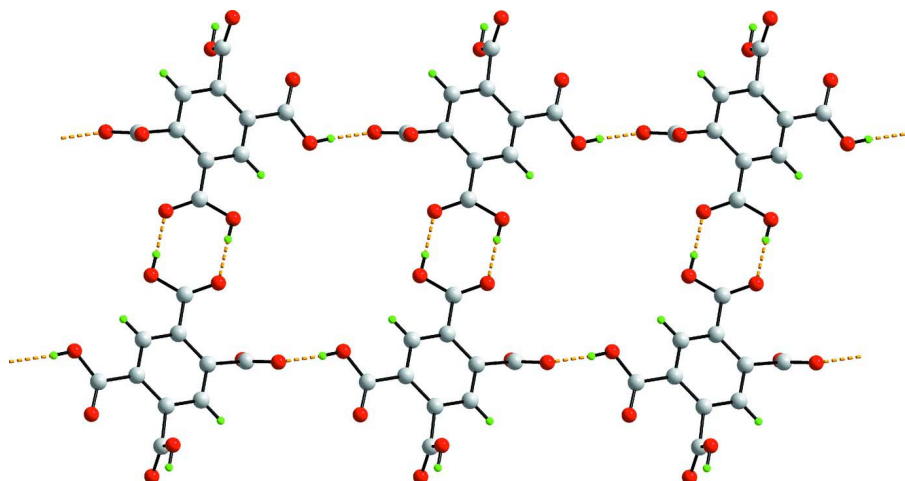
Crystals of the title salt hydrate were harvested from an ethanol (10 ml) solution containing a 1:1 molar ratio of pyromellitic acid (Sigma-Aldrich; 6 mg) and isonicotinic acid (Sigma-Aldrich; 3 mg).

S3. Refinement

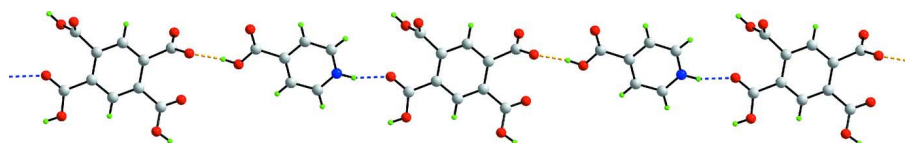
C-bound H-atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation with $U_{iso}(H)$ set to $1.2U_{eq}(C)$. The O—H and N—H atoms were located in difference maps and were refined with O—H = 0.84 ± 0.01 Å and N—H = 0.88 ± 0.01 Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$ and $U_{iso}(H) = 1.2U_{eq}(N)$, respectively.

**Figure 1**

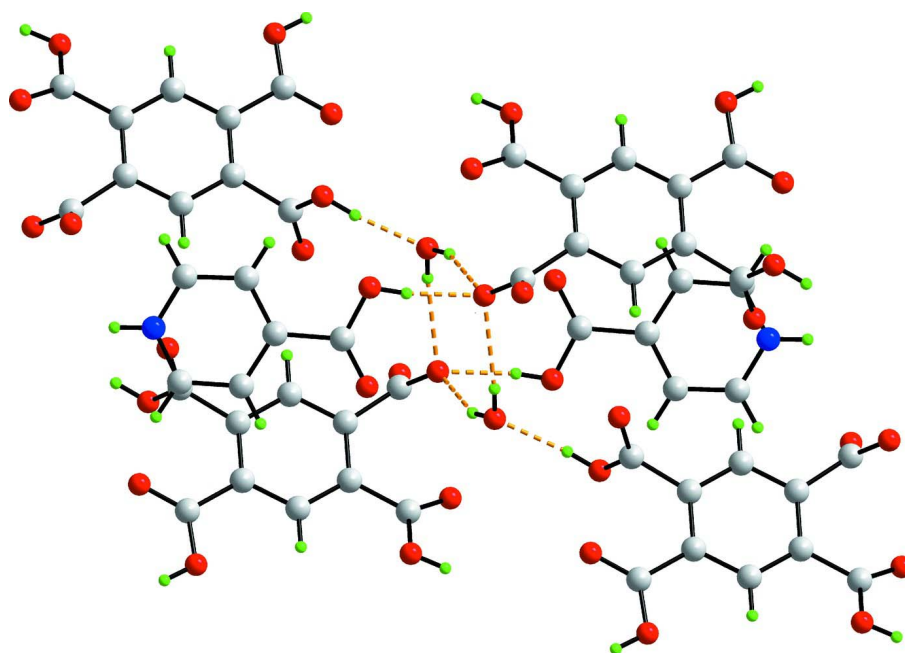
Molecular structures of (a) the 4-carboxypyridin-1-ium cation and (b) the hydroxy(2,4,5-tricarboxyphenyl)methanolate anion and water molecule (hydrogen bond shown as a dashed line) in (I), showing displacement ellipsoids at the 50% probability level.

**Figure 2**

Supramolecular tape mediated by O—H...O hydrogen bonding between anions. The O—H...O hydrogen bonds are shown as orange dashed lines.

**Figure 3**

Supramolecular chain mediated by N—H...O hydrogen bonding between cations and anions. The N—H...O hydrogen bonds are shown as blue dashed lines.

**Figure 4**

Detail of the hydrogen bonding involving the trifurcated carboxylate-O2 atom and water molecule of solvation.

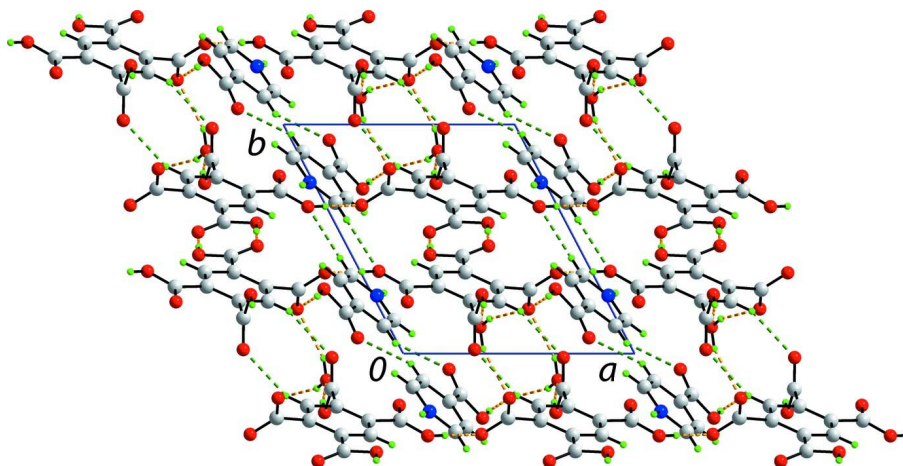


Figure 5

Unit-cell contents in (I) viewed in projection down the c axis. The C—H...O interactions are shown as green dashed lines.

4-Carboxypyridin-1-ium 2,4,5-tricarboxybenzoate monohydrate

Crystal data

$C_6H_6NO_2^+ \cdot C_{10}H_5O_8^- \cdot H_2O$

$M_r = 395.27$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 9.724$ (2) Å

$b = 10.007$ (2) Å

$c = 10.755$ (2) Å

$\alpha = 99.56$ (1)°

$\beta = 114.667$ (8)°

$\gamma = 110.283$ (9)°

$V = 830.7$ (3) Å³

$Z = 2$

$F(000) = 408$

$D_x = 1.580$ Mg m⁻³

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

Cell parameters from 3944 reflections

$\theta = 2.3$ – 29.8 °

$\mu = 0.14$ mm⁻¹

$T = 98$ K

Block, colourless

$0.33 \times 0.25 \times 0.20$ mm

Data collection

Rigaku AFC12K/SATURN724
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.807$, $T_{\max} = 1.000$

5233 measured reflections

3414 independent reflections

3200 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 26.5$ °, $\theta_{\min} = 2.3$ °

$h = -11 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.133$

$S = 1.17$

3414 reflections

281 parameters

8 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 1.2826P]$

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

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

$\Delta\rho_{\max} = 0.34$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ e Å⁻³

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1555 (2)	0.6476 (2)	0.60109 (18)	0.0198 (4)
O2	0.3582 (2)	0.80549 (19)	0.83497 (17)	0.0192 (4)
O3	0.3881 (2)	0.53016 (19)	0.85274 (17)	0.0180 (4)
O4	0.6609 (2)	0.56930 (19)	0.94793 (17)	0.0164 (3)
H4O	0.642 (4)	0.534 (4)	1.008 (3)	0.037 (9)*
O5	0.8655 (2)	0.7742 (2)	0.5022 (2)	0.0235 (4)
O6	0.9197 (2)	0.6410 (2)	0.64907 (19)	0.0210 (4)
H6O	0.994 (4)	0.643 (5)	0.627 (5)	0.076 (15)*
O7	0.6828 (2)	0.98272 (19)	0.46806 (18)	0.0198 (4)
O8	0.5263 (2)	0.7429 (2)	0.29663 (18)	0.0219 (4)
H8O	0.542 (6)	0.788 (5)	0.240 (4)	0.077 (15)*
O9	0.1620 (3)	0.9309 (3)	-0.0204 (3)	0.0409 (6)
O10	0.1966 (2)	0.7184 (2)	-0.0264 (2)	0.0251 (4)
H10O	0.243 (4)	0.751 (4)	-0.074 (3)	0.039 (9)*
O1W	0.6084 (2)	0.8838 (2)	0.1330 (2)	0.0251 (4)
H1W	0.645 (4)	0.9798 (13)	0.166 (3)	0.042 (10)*
H2W	0.549 (4)	0.849 (3)	0.0401 (11)	0.058 (12)*
N1	-0.0175 (3)	0.7469 (2)	0.3153 (2)	0.0187 (4)
H1N	-0.054 (4)	0.736 (4)	0.378 (3)	0.037 (9)*
C1	0.4428 (3)	0.7087 (2)	0.6751 (2)	0.0129 (4)
C2	0.5480 (3)	0.6444 (2)	0.7461 (2)	0.0126 (4)
C3	0.6741 (3)	0.6448 (2)	0.7146 (2)	0.0127 (4)
H3	0.7450	0.6024	0.7630	0.015*
C4	0.6972 (3)	0.7066 (2)	0.6129 (2)	0.0123 (4)
C5	0.5920 (3)	0.7703 (2)	0.5415 (2)	0.0128 (4)
C6	0.4668 (3)	0.7715 (2)	0.5742 (2)	0.0136 (4)
H6	0.3973	0.8155	0.5272	0.016*
C7	0.3075 (3)	0.7199 (3)	0.7072 (2)	0.0138 (4)
C8	0.5237 (3)	0.5753 (2)	0.8532 (2)	0.0134 (4)
C9	0.8360 (3)	0.7090 (2)	0.5826 (2)	0.0131 (4)
C10	0.6099 (3)	0.8443 (2)	0.4328 (2)	0.0132 (4)
C11	0.0918 (3)	0.7909 (3)	0.1229 (2)	0.0171 (5)
C12	0.0210 (3)	0.8792 (3)	0.1604 (3)	0.0202 (5)
H12	0.0106	0.9548	0.1194	0.024*
C13	-0.0339 (3)	0.8546 (3)	0.2584 (3)	0.0215 (5)

H13	-0.0827	0.9131	0.2853	0.026*
C14	0.0488 (3)	0.6591 (3)	0.2804 (3)	0.0199 (5)
H14	0.0573	0.5842	0.3229	0.024*
C15	0.1047 (3)	0.6786 (3)	0.1820 (3)	0.0194 (5)
H15	0.1508	0.6169	0.1555	0.023*
C16	0.1542 (3)	0.8213 (3)	0.0175 (3)	0.0222 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0155 (8)	0.0324 (9)	0.0186 (8)	0.0140 (7)	0.0122 (7)	0.0092 (7)
O2	0.0233 (9)	0.0281 (9)	0.0162 (8)	0.0155 (7)	0.0150 (7)	0.0089 (7)
O3	0.0172 (8)	0.0267 (9)	0.0195 (8)	0.0122 (7)	0.0138 (7)	0.0133 (7)
O4	0.0156 (8)	0.0248 (8)	0.0150 (8)	0.0103 (7)	0.0104 (7)	0.0122 (7)
O5	0.0293 (10)	0.0366 (10)	0.0315 (10)	0.0243 (8)	0.0261 (8)	0.0242 (8)
O6	0.0232 (9)	0.0355 (10)	0.0279 (9)	0.0227 (8)	0.0213 (8)	0.0218 (8)
O7	0.0232 (9)	0.0193 (8)	0.0222 (9)	0.0103 (7)	0.0146 (7)	0.0108 (7)
O8	0.0294 (9)	0.0236 (9)	0.0135 (8)	0.0100 (8)	0.0128 (7)	0.0083 (7)
O9	0.0678 (16)	0.0473 (13)	0.0561 (14)	0.0395 (12)	0.0537 (13)	0.0393 (11)
O10	0.0327 (10)	0.0353 (10)	0.0244 (9)	0.0202 (9)	0.0230 (8)	0.0163 (8)
O1W	0.0305 (10)	0.0285 (10)	0.0195 (9)	0.0134 (8)	0.0150 (8)	0.0113 (8)
N1	0.0184 (10)	0.0241 (10)	0.0143 (9)	0.0065 (8)	0.0121 (8)	0.0060 (8)
C1	0.0124 (10)	0.0155 (10)	0.0121 (10)	0.0061 (8)	0.0083 (8)	0.0034 (8)
C2	0.0130 (10)	0.0158 (10)	0.0115 (10)	0.0078 (8)	0.0074 (8)	0.0050 (8)
C3	0.0129 (10)	0.0156 (10)	0.0133 (10)	0.0081 (8)	0.0081 (8)	0.0065 (8)
C4	0.0127 (10)	0.0146 (10)	0.0133 (10)	0.0076 (8)	0.0088 (8)	0.0046 (8)
C5	0.0136 (10)	0.0155 (10)	0.0102 (9)	0.0067 (8)	0.0070 (8)	0.0045 (8)
C6	0.0145 (10)	0.0183 (10)	0.0142 (10)	0.0106 (9)	0.0094 (9)	0.0073 (8)
C7	0.0178 (11)	0.0191 (11)	0.0156 (10)	0.0123 (9)	0.0129 (9)	0.0111 (9)
C8	0.0158 (10)	0.0150 (10)	0.0130 (10)	0.0079 (8)	0.0101 (9)	0.0044 (8)
C9	0.0127 (10)	0.0190 (11)	0.0133 (10)	0.0088 (9)	0.0098 (8)	0.0066 (8)
C10	0.0118 (10)	0.0198 (11)	0.0148 (10)	0.0107 (9)	0.0088 (8)	0.0089 (9)
C11	0.0172 (11)	0.0208 (11)	0.0147 (10)	0.0075 (9)	0.0104 (9)	0.0064 (9)
C12	0.0212 (12)	0.0207 (11)	0.0202 (11)	0.0093 (10)	0.0118 (10)	0.0081 (9)
C13	0.0213 (12)	0.0244 (12)	0.0220 (12)	0.0117 (10)	0.0138 (10)	0.0057 (10)
C14	0.0217 (12)	0.0233 (12)	0.0187 (11)	0.0103 (10)	0.0129 (10)	0.0097 (9)
C15	0.0218 (12)	0.0255 (12)	0.0187 (11)	0.0140 (10)	0.0135 (10)	0.0098 (10)
C16	0.0260 (13)	0.0313 (13)	0.0200 (11)	0.0160 (11)	0.0168 (10)	0.0135 (10)

Geometric parameters (Å, °)

O1—C7	1.260 (3)	C1—C2	1.418 (3)
O2—C7	1.271 (3)	C1—C7	1.528 (3)
O3—C8	1.234 (3)	C2—C3	1.400 (3)
O4—C8	1.327 (3)	C2—C8	1.497 (3)
O4—H4O	0.845 (10)	C3—C4	1.401 (3)
O5—C9	1.232 (3)	C3—H3	0.9500
O6—C9	1.303 (3)	C4—C5	1.415 (3)

O6—H6O	0.847 (10)	C4—C9	1.509 (3)
O7—C10	1.219 (3)	C5—C6	1.404 (3)
O8—C10	1.333 (3)	C5—C10	1.521 (3)
O8—H8O	0.846 (10)	C6—H6	0.9500
O9—C16	1.221 (3)	C11—C15	1.397 (3)
O10—C16	1.323 (3)	C11—C12	1.398 (3)
O10—H10O	0.845 (10)	C11—C16	1.519 (3)
O1W—H1W	0.849 (10)	C12—C13	1.386 (3)
O1W—H2W	0.847 (10)	C12—H12	0.9500
N1—C13	1.347 (3)	C13—H13	0.9500
N1—C14	1.347 (3)	C14—C15	1.389 (3)
N1—H1N	0.885 (10)	C14—H14	0.9500
C1—C6	1.401 (3)	C15—H15	0.9500
C8—O4—H4O	110 (2)	O2—C7—C1	117.70 (19)
C9—O6—H6O	111 (3)	O3—C8—O4	124.0 (2)
C10—O8—H8O	110 (3)	O3—C8—C2	122.2 (2)
C16—O10—H10O	106 (2)	O4—C8—C2	113.81 (18)
H1W—O1W—H2W	109.7 (16)	O5—C9—O6	124.6 (2)
C13—N1—C14	123.1 (2)	O5—C9—C4	120.44 (19)
C13—N1—H1N	116 (2)	O6—C9—C4	114.93 (18)
C14—N1—H1N	121 (2)	O7—C10—O8	125.1 (2)
C6—C1—C2	119.26 (19)	O7—C10—C5	121.98 (19)
C6—C1—C7	117.27 (19)	O8—C10—C5	112.69 (18)
C2—C1—C7	123.42 (19)	C15—C11—C12	120.4 (2)
C3—C2—C1	119.65 (19)	C15—C11—C16	121.5 (2)
C3—C2—C8	120.08 (19)	C12—C11—C16	118.1 (2)
C1—C2—C8	120.27 (19)	C13—C12—C11	118.8 (2)
C2—C3—C4	121.0 (2)	C13—C12—H12	120.6
C2—C3—H3	119.5	C11—C12—H12	120.6
C4—C3—H3	119.5	N1—C13—C12	119.5 (2)
C3—C4—C5	119.42 (19)	N1—C13—H13	120.2
C3—C4—C9	120.37 (19)	C12—C13—H13	120.2
C5—C4—C9	120.19 (19)	N1—C14—C15	119.7 (2)
C6—C5—C4	119.57 (19)	N1—C14—H14	120.2
C6—C5—C10	116.79 (19)	C15—C14—H14	120.2
C4—C5—C10	123.60 (19)	C14—C15—C11	118.5 (2)
C5—C6—C1	121.1 (2)	C14—C15—H15	120.7
C5—C6—H6	119.5	C11—C15—H15	120.7
C1—C6—H6	119.5	O9—C16—O10	125.4 (2)
O1—C7—O2	126.2 (2)	O9—C16—C11	121.5 (2)
O1—C7—C1	116.06 (19)	O10—C16—C11	113.1 (2)
C6—C1—C2—C3	0.1 (3)	C3—C2—C8—O4	23.1 (3)
C7—C1—C2—C3	-177.2 (2)	C1—C2—C8—O4	-157.40 (19)
C6—C1—C2—C8	-179.41 (19)	C3—C4—C9—O5	-174.1 (2)
C7—C1—C2—C8	3.3 (3)	C5—C4—C9—O5	4.3 (3)
C1—C2—C3—C4	-0.6 (3)	C3—C4—C9—O6	4.6 (3)

C8—C2—C3—C4	178.9 (2)	C5—C4—C9—O6	-177.0 (2)
C2—C3—C4—C5	0.3 (3)	C6—C5—C10—O7	77.3 (3)
C2—C3—C4—C9	178.74 (19)	C4—C5—C10—O7	-100.5 (3)
C3—C4—C5—C6	0.4 (3)	C6—C5—C10—O8	-97.4 (2)
C9—C4—C5—C6	-178.04 (19)	C4—C5—C10—O8	84.8 (3)
C3—C4—C5—C10	178.15 (19)	C15—C11—C12—C13	0.8 (4)
C9—C4—C5—C10	-0.3 (3)	C16—C11—C12—C13	-178.9 (2)
C4—C5—C6—C1	-0.9 (3)	C14—N1—C13—C12	-0.7 (4)
C10—C5—C6—C1	-178.77 (19)	C11—C12—C13—N1	0.1 (4)
C2—C1—C6—C5	0.6 (3)	C13—N1—C14—C15	0.3 (4)
C7—C1—C6—C5	178.1 (2)	N1—C14—C15—C11	0.6 (4)
C6—C1—C7—O1	64.6 (3)	C12—C11—C15—C14	-1.2 (4)
C2—C1—C7—O1	-118.1 (2)	C16—C11—C15—C14	178.6 (2)
C6—C1—C7—O2	-112.4 (2)	C15—C11—C16—O9	-171.1 (3)
C2—C1—C7—O2	64.9 (3)	C12—C11—C16—O9	8.7 (4)
C3—C2—C8—O3	-157.6 (2)	C15—C11—C16—O10	9.1 (3)
C1—C2—C8—O3	21.9 (3)	C12—C11—C16—O10	-171.2 (2)

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>
O4—H4O...O3 ⁱ	0.84 (3)	1.82 (3)	2.654 (3)	176 (3)
O6—H6O...O1 ⁱⁱ	0.85 (5)	1.69 (5)	2.534 (3)	174 (5)
O8—H8O...O1 ^W	0.85 (5)	1.79 (5)	2.634 (3)	171 (6)
O10—H10O...O2 ⁱⁱⁱ	0.85 (4)	1.78 (4)	2.625 (3)	172 (4)
N1—H1N...O5 ^{iv}	0.89 (4)	1.86 (4)	2.711 (3)	160 (4)
O1 ^W —H1 ^W ...O2 ^v	0.85 (2)	2.16 (2)	2.957 (3)	156 (3)
O1 ^W —H2 ^W ...O2 ⁱⁱⁱ	0.85 (1)	2.05 (2)	2.853 (3)	158 (4)
C6—H6...O7 ^v	0.95	2.40	3.267 (3)	151
C12—H12...O9 ^{vi}	0.95	2.35	3.179 (4)	146
C14—H14...O6 ^{vii}	0.95	2.40	3.300 (4)	159

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