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2,9-Dimethyl-1,10-phenanthrolin-1-ium 2,4,5-tricarboxybenzoate monohydrate

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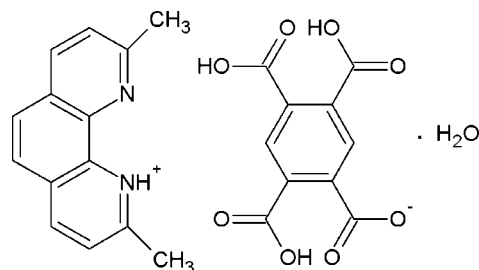
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Key indicators: single-crystal X-ray study; $T = 223$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
R factor = 0.088; wR factor = 0.272; data-to-parameter ratio = 13.8.

In the preparation of the title hydrated salt, $\text{C}_{14}\text{H}_{13}\text{N}_2^+ \cdot \text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{H}_2\text{O}$, a proton has been transferred to the 2,9-dimethyl-1,10-phenanthrolinium cation, forming a 2,4,5-tricarboxybenzoate anion. In the anion, the mean planes of the protonated carboxylate groups form dihedral angles of 11.0 (5), 4.4 (5) and 80.3 (4)° with the benzene ring to which they are attached. The mean plane of the deprotonated carboxylate group forms a dihedral angle of 10.6 (5)° with the benzene ring. In the crystal, the anions are involved in carboxylic acid $\text{O}-\text{H} \cdots \text{O}_{\text{carboxyl}}$ hydrogen bonds, generating a two-dimensional network parallel to (001) containing $R_4^4(28)$ and $R_4^4(32)$ motifs. The 2,9-dimethyl-1,10-phenanthrolinium cations and water molecules reside between the anion layers and are connected to the anions *via* $\text{N}-\text{H} \cdots \text{O}_{\text{water}}$ and $\text{O}_{\text{water}}-\text{H} \cdots \text{O}_{\text{carboxyl}}$ hydrogen bonds. An intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond is also observed in the anion.

Related literature

For related structures, see: Adams & Ramdas (1978); Mrvos-Sermek *et al.* (1996); Sun *et al.* (2002a,b); Zhu *et al.* (2002); Li *et al.* (2003; 2006); Oscar *et al.* (2008). For background to molecular recognition and supramolecular chemistry, see: Batten & Robson (1998); Juan *et al.* (2002); Qiu *et al.* (2008). For hydrogen-bond graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{13}\text{N}_2^+ \cdot \text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{H}_2\text{O}$
 $M_r = 480.42$
Orthorhombic, *Pbca*
 $a = 7.1135$ (8) Å
 $b = 19.4512$ (11) Å
 $c = 30.800$ (2) Å

$V = 4261.7$ (6) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 223$ K
0.35 × 0.20 × 0.15 mm

Data collection

Rigaku Mercury CCD
diffractometer
Absorption correction: multi-scan
(*REQAB*; Jacobson, 1998)
 $T_{\text{min}} = 0.468$, $T_{\text{max}} = 1.000$

19580 measured reflections
4346 independent reflections
2278 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.173$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.088$
 $wR(F^2) = 0.272$
 $S = 1.00$
4346 reflections
316 parameters

3 restraints
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| $\text{O2}-\text{H2} \cdots \text{O3}$ | 0.82 | 1.58 | 2.395 (4) | 171 |
| $\text{O5}-\text{H5} \cdots \text{O1}^{\text{i}}$ | 0.82 | 1.86 | 2.671 (3) | 172 |
| $\text{O8}-\text{H8} \cdots \text{O3}^{\text{ii}}$ | 0.82 | 1.82 | 2.645 (4) | 178 |
| $\text{N1}-\text{H1A} \cdots \text{O1W}^{\text{iii}}$ | 0.86 | 1.92 | 2.738 (4) | 160 |
| $\text{O1W}-\text{H1WA} \cdots \text{O4}^{\text{ii}}$ | 0.82 | 1.92 | 2.735 (4) | 171 |
| $\text{O1W}-\text{H1WB} \cdots \text{O7}^{\text{iv}}$ | 0.82 | 2.11 | 2.873 (4) | 155 |

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

Data collection: *CrystalClear* (Rigaku, 2007); 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: *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5664).

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supporting information

Acta Cryst. (2013). E69, o1782–o1783 [doi:10.1107/S1600536813030857]

2,9-Dimethyl-1,10-phenanthroline-1-ium 2,4,5-tricarboxybenzoate monohydrate

Kai-Long Zhong

S1. Comment

It is well established that hydrogen bonds play vital roles in molecular recognition and supramolecular chemistry (Batten & Robson 1998; Juan *et al.*, 2002; Qiu *et al.*, 2008), owing to their moderately directional intermolecular interaction which can effectively control short-range packing. 1,2,4,5-Benzenetetracarboxylic acid (Li *et al.*, 2003; Oscar *et al.*, 2008) has been widely applied in constructing interesting supramolecular networks because it acts not only as hydrogen bond acceptor but also as a hydrogen bond donor, depending upon the number of deprotonated carboxylate groups. Some proton-transfer compounds of 1,2,4,5-benzenetetracarboxylic acid with nitrogen Lewis bases, such as guanidinium pyromellitate trihydrate monoperhydrate (Adams & Ramdas, 1978), 2,2'-bipyridinium hemi[1,2,4,5-benzenetetracarboxylate(2-)] hemi(1,2,4,5-benzenetetracarboxylic acid) (Mrvos-Sermek *et al.*, 1996), guanidinium 2,9-dimethyl-1,10-phenanthroline trihydrogen-1,2,3,4-tetracarboxybenzoate monohydrate (Sun *et al.*, 2002*a*), imidazolium trihydrogen-1,2,4,5-benzenetetracarboxylate (Sun *et al.*, 2002*b*), 6,21-diaza-3,9,18,24-tetraazoniatricyclo[22.2.2.2^{11,14}] triaconta-11,13,24,26 (1),27,29-hexaene benzene-1,2,4,5-tetracarboxylate(4-) hexahydrate (Zhu *et al.*, 2002) and ethylenediammonium bis(trihydrogen-1,2,4,5-benzenetetracarboxylate) dehydrate (Li *et al.*, 2006) have been synthesized and reported. The title compound (I) was obtained unintentionally during an attempt to synthesize mixed-ligand transition metal complexes with 1,2,4,5-benzenetetracarboxylic acid and 2,9-dimethyl-1,10-phenanthroline ligands *via* a solvo thermal reaction. Its crystal structure is reported herein.

The asymmetric unit of (I) (Fig. 1) is comprised of a 2,9-dimethyl-1,10-phenanthroline cation, a trihydrogen-1,2,4,5-benzenetetracarboxylate anion and a solvent water molecule. The proton transfer from a carboxyl group to the ring N atom (N1) of the 2,9-dimethyl-1,10-phenanthroline is manifested in an increased internal angle [C1—N1—C12 = 123.7 (3)°] of the pyridine ring, compared with that for atom N2 of the pyridine ring [C10—N2—C11 = 117.8 (3)°]. The protonation diminishes the steric effect of the lone pair of electrons and is responsible for the slightly increased C1—N1—C12 angle. In the anion, the mean-planes of the protonated carboxylate groups form dihedral angles of 11.0 (5)° for C34/O1/O2, 4.4 (5)° for C36/O5/O6 and 80.3 (4)° for C37/O7/O8, with the benzene ring to which they are attached. The mean-plane of the deprotonated carboxylate group C35/O4/O4 forms a dihedral angle of 10.6 (5)° with the benzene ring. Symmetry-related trihydrogen-1,2,4,5-benzenetetracarboxylate anions interact *via* O5—H5[⋯]O1ⁱ and O8—H8[⋯]O3ⁱⁱ hydrogen bonds, forming a two-dimensional supramolecular layer parallel to (001), which involves $R_4^4(28)$ and $R_4^4(32)$ motifs (Bernstein *et al.*, 1995) (Fig. 2 & Table 1). The 2,9-dimethyl-1,10-phenanthroline cations are linked to the water molecules (O1W) through N1—H1A[⋯]O1Wⁱⁱⁱ hydrogen bonds and reside between the two-dimensional supramolecular layers and are connected to the layers *via* O1W—H1WA[⋯]O4ⁱⁱ and O1W—H1WB[⋯]O7^{iv} hydrogen bonds (Fig. 3 & Table 1).

S2. Experimental

2,9-Dimethyl-1,10-phenanthroline (0.1 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.1 mmol), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.1 mmol) and 2.0 ml water were mixed and placed in a thick Pyrex tube, which was sealed and heated to 383 K for 72 h, whereupon colorless block-shaped crystals of (I) were obtained.

S3. Refinement

The H atoms bonded to C atoms were positioned geometrically and allowed to ride on their parent atoms, with $\text{C}-\text{H} = 0.93, 0.96 \text{ \AA}$; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. The H atoms bound to N and O were placed in calculated positions with $\text{N}-\text{H} = 0.86 \text{ \AA}$, $\text{O}-\text{H} = 0.82 \text{ \AA}$ and refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The precision of the structure is slightly lower than normal as reflected in the R-factors. We attempted to use several crystals but the crystal used to collect the data herein was the best quality available.

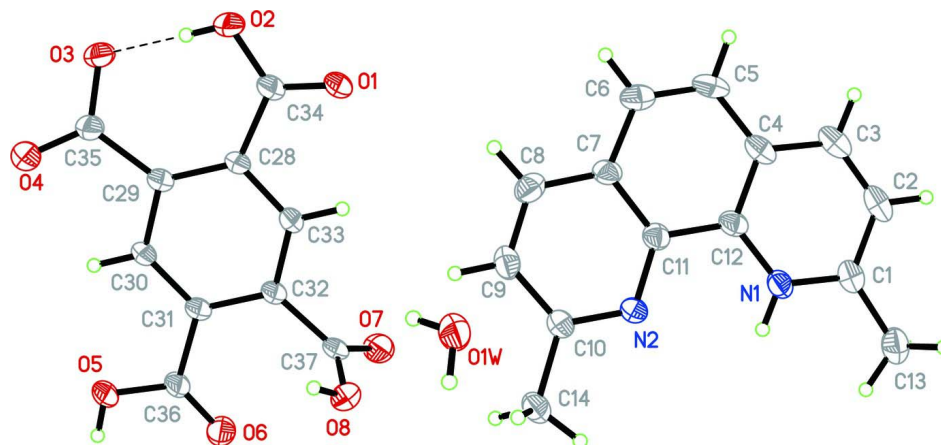


Figure 1

The asymmetric unit of (I), showing displacement ellipsoids drawn at the 30% probability level. An intramolecular hydrogen bond is shown as a dashed line.

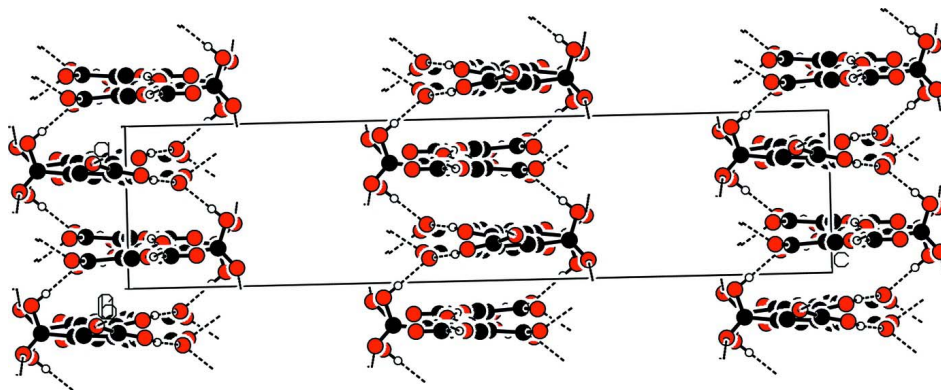
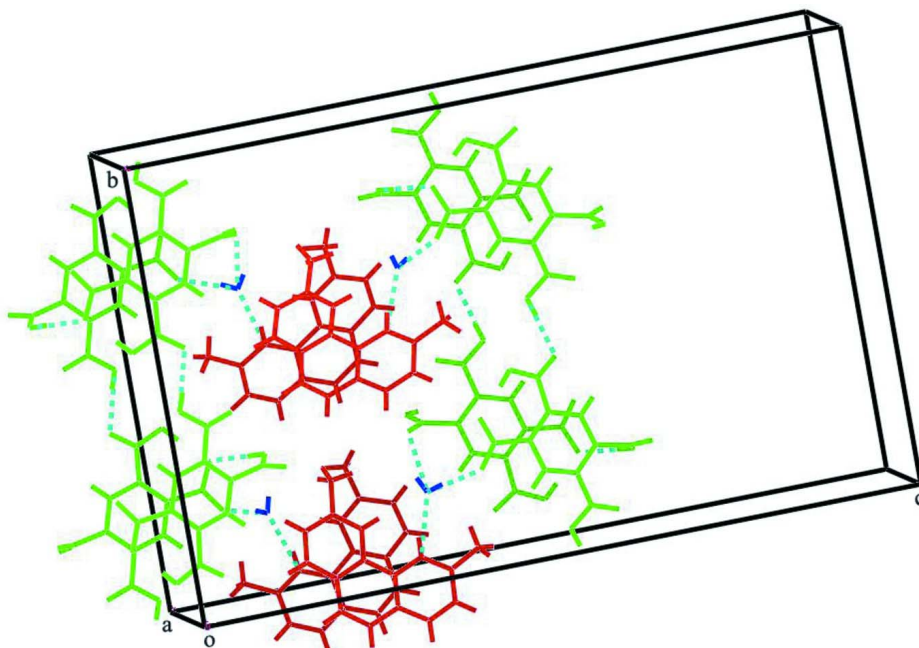


Figure 2

Part of the crystal structure of (I) showing layers parallel to (0 0 1). Hydrogen bonds are represented by dashed lines. The 2,9-dimethyl-1,10-phenanthroline cations and the water molecules have been omitted for clarity.

**Figure 3**

Part of the crystal structure showing hydrogen bonds involving the cations (red) and water molecules (blue). The hydrogen bond donor...acceptor distances are shown as dashed lines.

2,9-Dimethyl-1,10-phenanthroline-1-ium 2,4,5-tricarboxybenzoate monohydrate

Crystal data

$C_{14}H_{13}N_2^+ \cdot C_{10}H_5O_8^- \cdot H_2O$

$M_r = 480.42$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 7.1135$ (8) Å

$b = 19.4512$ (11) Å

$c = 30.800$ (2) Å

$V = 4261.7$ (6) Å³

$Z = 8$

$F(000) = 2000$

$D_x = 1.498$ Mg m⁻³

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

Cell parameters from 2016 reflections

$\theta = 3.4$ – 26.0°

$\mu = 0.12$ mm⁻¹

$T = 223$ K

Block, colourless

$0.35 \times 0.20 \times 0.15$ mm

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite Monochromator monochromator

Detector resolution: 28.5714 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*REQAB*; Jacobson, 1998)

$T_{\min} = 0.468$, $T_{\max} = 1.000$

19580 measured reflections

4346 independent reflections

2278 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.173$

$\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -8 \rightarrow 7$

$k = -24 \rightarrow 23$

$l = -38 \rightarrow 30$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.088$
 $wR(F^2) = 0.272$
 $S = 1.00$
 4346 reflections
 316 parameters
 3 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1341P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|---------------|---------------|----------------------------------|
| O1 | 0.2749 (5) | 0.08753 (12) | 0.04898 (9) | 0.0620 (10) |
| O1W | 0.9045 (6) | 0.17263 (15) | 0.15048 (10) | 0.0773 (11) |
| H1WA | 0.8321 | 0.1863 | 0.1316 | 0.116* |
| H1WB | 0.9732 | 0.2039 | 0.1586 | 0.116* |
| O2 | 0.1964 (5) | 0.09431 (13) | -0.01923 (9) | 0.0687 (11) |
| H2 | 0.1669 | 0.1239 | -0.0369 | 0.103* |
| O3 | 0.1453 (4) | 0.18081 (12) | -0.07332 (9) | 0.0514 (8) |
| O4 | 0.1828 (5) | 0.29265 (13) | -0.08131 (10) | 0.0607 (9) |
| O5 | 0.1946 (5) | 0.45577 (12) | 0.02561 (9) | 0.0710 (11) |
| H5 | 0.1941 | 0.4958 | 0.0340 | 0.106* |
| O6 | 0.1961 (6) | 0.43455 (14) | 0.09547 (10) | 0.0814 (12) |
| O7 | 0.1129 (5) | 0.29909 (14) | 0.15299 (9) | 0.0570 (9) |
| O8 | 0.4094 (5) | 0.32175 (13) | 0.13965 (9) | 0.0526 (8) |
| H8 | 0.4812 | 0.3203 | 0.1189 | 0.079* |
| N1 | 0.3348 (5) | 0.04067 (14) | 0.32309 (11) | 0.0418 (8) |
| H1A | 0.3756 | 0.0820 | 0.3261 | 0.050* |
| N2 | 0.4269 (5) | 0.12165 (13) | 0.25335 (10) | 0.0387 (8) |
| C1 | 0.2968 (6) | 0.0044 (2) | 0.35906 (14) | 0.0505 (11) |
| C2 | 0.2298 (6) | -0.0628 (2) | 0.35368 (16) | 0.0565 (12) |
| H2B | 0.2018 | -0.0892 | 0.3780 | 0.068* |
| C3 | 0.2051 (6) | -0.0901 (2) | 0.31345 (16) | 0.0540 (12) |
| H3A | 0.1608 | -0.1348 | 0.3107 | 0.065* |
| C4 | 0.2457 (6) | -0.05151 (18) | 0.27592 (15) | 0.0464 (10) |
| C5 | 0.2205 (6) | -0.07699 (19) | 0.23280 (16) | 0.0510 (11) |
| H5A | 0.1792 | -0.1218 | 0.2285 | 0.061* |

| | | | | |
|------|------------|--------------|---------------|-------------|
| C6 | 0.2559 (6) | -0.0366 (2) | 0.19861 (16) | 0.0498 (11) |
| H6A | 0.2354 | -0.0539 | 0.1709 | 0.060* |
| C7 | 0.3240 (6) | 0.03194 (17) | 0.20314 (13) | 0.0403 (9) |
| C8 | 0.3644 (6) | 0.0762 (2) | 0.16851 (14) | 0.0488 (10) |
| H8A | 0.3421 | 0.0621 | 0.1401 | 0.059* |
| C9 | 0.4360 (6) | 0.13951 (19) | 0.17649 (13) | 0.0473 (10) |
| H9A | 0.4648 | 0.1686 | 0.1535 | 0.057* |
| C10 | 0.4672 (6) | 0.16161 (16) | 0.21950 (12) | 0.0416 (10) |
| C11 | 0.3565 (5) | 0.05828 (17) | 0.24523 (12) | 0.0382 (9) |
| C12 | 0.3122 (5) | 0.01557 (17) | 0.28188 (13) | 0.0397 (10) |
| C13 | 0.3258 (8) | 0.0376 (2) | 0.40228 (16) | 0.0716 (15) |
| H13A | 0.3728 | 0.0834 | 0.3982 | 0.107* |
| H13B | 0.4149 | 0.0113 | 0.4188 | 0.107* |
| H13C | 0.2084 | 0.0394 | 0.4176 | 0.107* |
| C14 | 0.5500 (6) | 0.23092 (17) | 0.22864 (14) | 0.0505 (11) |
| H14A | 0.5598 | 0.2375 | 0.2595 | 0.076* |
| H14B | 0.4706 | 0.2659 | 0.2165 | 0.076* |
| H14C | 0.6728 | 0.2338 | 0.2158 | 0.076* |
| C28 | 0.2079 (5) | 0.20013 (15) | 0.02367 (12) | 0.0357 (9) |
| C29 | 0.1912 (5) | 0.25062 (16) | -0.00893 (13) | 0.0350 (9) |
| C30 | 0.1867 (5) | 0.31977 (17) | 0.00395 (12) | 0.0378 (9) |
| H30A | 0.1756 | 0.3535 | -0.0173 | 0.045* |
| C31 | 0.1979 (5) | 0.33993 (16) | 0.04710 (12) | 0.0376 (9) |
| C32 | 0.2144 (6) | 0.28974 (16) | 0.07952 (12) | 0.0389 (10) |
| C33 | 0.2186 (6) | 0.22157 (17) | 0.06673 (12) | 0.0394 (9) |
| H33A | 0.2291 | 0.1881 | 0.0881 | 0.047* |
| C34 | 0.2288 (7) | 0.12280 (18) | 0.01805 (14) | 0.0471 (11) |
| C35 | 0.1756 (6) | 0.24134 (18) | -0.05812 (13) | 0.0411 (10) |
| C36 | 0.1967 (6) | 0.41454 (17) | 0.05910 (13) | 0.0457 (11) |
| C37 | 0.2376 (7) | 0.30587 (16) | 0.12675 (13) | 0.0428 (10) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-----------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.119 (3) | 0.0212 (13) | 0.0460 (18) | 0.0077 (14) | -0.0028 (17) | -0.0004 (12) |
| O1W | 0.107 (3) | 0.066 (2) | 0.058 (2) | -0.0367 (18) | -0.023 (2) | 0.0200 (15) |
| O2 | 0.131 (3) | 0.0301 (14) | 0.0452 (18) | 0.0046 (16) | -0.0161 (18) | -0.0095 (13) |
| O3 | 0.077 (2) | 0.0359 (14) | 0.0416 (17) | 0.0044 (13) | -0.0108 (15) | -0.0086 (12) |
| O4 | 0.095 (3) | 0.0408 (16) | 0.0464 (18) | -0.0027 (14) | -0.0044 (17) | 0.0012 (14) |
| O5 | 0.149 (4) | 0.0180 (13) | 0.0458 (19) | -0.0050 (15) | -0.0022 (19) | 0.0033 (12) |
| O6 | 0.171 (4) | 0.0306 (15) | 0.0427 (19) | 0.0046 (17) | 0.000 (2) | -0.0069 (14) |
| O7 | 0.075 (2) | 0.0492 (17) | 0.0465 (18) | -0.0069 (14) | 0.0186 (17) | -0.0076 (13) |
| O8 | 0.072 (2) | 0.0489 (15) | 0.0371 (16) | -0.0054 (14) | -0.0002 (15) | -0.0068 (12) |
| N1 | 0.054 (2) | 0.0278 (15) | 0.044 (2) | 0.0022 (14) | 0.0008 (16) | 0.0035 (14) |
| N2 | 0.048 (2) | 0.0261 (14) | 0.0421 (19) | 0.0036 (13) | -0.0007 (16) | 0.0003 (13) |
| C1 | 0.057 (3) | 0.042 (2) | 0.053 (3) | 0.0034 (19) | -0.001 (2) | 0.0130 (19) |
| C2 | 0.059 (3) | 0.040 (2) | 0.071 (3) | 0.005 (2) | 0.006 (3) | 0.022 (2) |
| C3 | 0.052 (3) | 0.033 (2) | 0.078 (3) | 0.0028 (18) | 0.009 (2) | 0.009 (2) |

| | | | | | | |
|-----|-----------|-------------|-----------|--------------|--------------|--------------|
| C4 | 0.043 (2) | 0.0283 (18) | 0.068 (3) | 0.0023 (16) | 0.001 (2) | 0.0029 (19) |
| C5 | 0.046 (3) | 0.030 (2) | 0.077 (3) | -0.0055 (17) | -0.003 (2) | -0.014 (2) |
| C6 | 0.051 (3) | 0.043 (2) | 0.056 (3) | 0.0024 (19) | -0.001 (2) | -0.016 (2) |
| C7 | 0.045 (2) | 0.0305 (19) | 0.045 (2) | 0.0050 (15) | -0.0001 (19) | -0.0067 (17) |
| C8 | 0.054 (3) | 0.053 (2) | 0.039 (2) | 0.008 (2) | -0.002 (2) | -0.0088 (19) |
| C9 | 0.056 (3) | 0.043 (2) | 0.044 (2) | 0.0074 (19) | 0.005 (2) | 0.0094 (18) |
| C10 | 0.049 (3) | 0.0318 (17) | 0.044 (2) | 0.0032 (16) | -0.0029 (19) | 0.0021 (16) |
| C11 | 0.042 (2) | 0.0335 (18) | 0.039 (2) | 0.0060 (16) | 0.0018 (18) | -0.0017 (16) |
| C12 | 0.040 (2) | 0.0285 (18) | 0.051 (3) | 0.0043 (15) | -0.0003 (19) | -0.0022 (17) |
| C13 | 0.109 (5) | 0.058 (3) | 0.048 (3) | 0.000 (3) | -0.002 (3) | 0.015 (2) |
| C14 | 0.066 (3) | 0.034 (2) | 0.052 (3) | -0.0008 (19) | 0.004 (2) | 0.0064 (18) |
| C28 | 0.047 (2) | 0.0222 (17) | 0.038 (2) | -0.0023 (14) | -0.0021 (17) | -0.0018 (15) |
| C29 | 0.041 (2) | 0.0259 (17) | 0.038 (2) | -0.0004 (15) | 0.0001 (17) | -0.0025 (15) |
| C30 | 0.051 (3) | 0.0236 (17) | 0.039 (2) | -0.0029 (16) | -0.0039 (18) | 0.0019 (15) |
| C31 | 0.051 (3) | 0.0217 (16) | 0.040 (2) | 0.0003 (15) | 0.0012 (18) | -0.0030 (15) |
| C32 | 0.057 (3) | 0.0230 (17) | 0.037 (2) | -0.0001 (15) | 0.0026 (18) | -0.0014 (15) |
| C33 | 0.056 (3) | 0.0260 (17) | 0.036 (2) | -0.0019 (16) | 0.0024 (19) | 0.0029 (15) |
| C34 | 0.071 (3) | 0.0235 (18) | 0.047 (2) | -0.0011 (17) | 0.007 (2) | -0.0012 (18) |
| C35 | 0.050 (3) | 0.033 (2) | 0.040 (2) | 0.0016 (16) | -0.0026 (19) | -0.0037 (17) |
| C36 | 0.074 (3) | 0.0215 (18) | 0.041 (2) | 0.0029 (17) | 0.005 (2) | -0.0009 (17) |
| C37 | 0.070 (3) | 0.0175 (16) | 0.041 (2) | -0.0042 (17) | -0.002 (2) | -0.0005 (16) |

Geometric parameters (Å, °)

| | | | |
|----------|-----------|----------|-----------|
| O1—C34 | 1.219 (5) | C6—C7 | 1.426 (5) |
| O1W—H1WA | 0.8199 | C6—H6A | 0.9300 |
| O1W—H1WB | 0.8200 | C7—C8 | 1.400 (6) |
| O2—C34 | 1.296 (5) | C7—C11 | 1.413 (5) |
| O2—H2 | 0.8200 | C8—C9 | 1.356 (5) |
| O3—C35 | 1.285 (4) | C8—H8A | 0.9300 |
| O4—C35 | 1.228 (5) | C9—C10 | 1.410 (5) |
| O5—C36 | 1.307 (5) | C9—H9A | 0.9300 |
| O5—H5 | 0.8200 | C10—C14 | 1.498 (5) |
| O6—C36 | 1.186 (5) | C11—C12 | 1.436 (5) |
| O7—C37 | 1.208 (5) | C13—H13A | 0.9600 |
| O8—C37 | 1.321 (5) | C13—H13B | 0.9600 |
| O8—H8 | 0.8200 | C13—H13C | 0.9600 |
| N1—C1 | 1.341 (5) | C14—H14A | 0.9600 |
| N1—C12 | 1.369 (5) | C14—H14B | 0.9600 |
| N1—H1A | 0.8600 | C14—H14C | 0.9600 |
| N2—C10 | 1.331 (4) | C28—C33 | 1.392 (5) |
| N2—C11 | 1.354 (5) | C28—C29 | 1.409 (5) |
| C1—C2 | 1.401 (6) | C28—C34 | 1.521 (5) |
| C1—C13 | 1.494 (6) | C29—C30 | 1.403 (5) |
| C2—C3 | 1.359 (6) | C29—C35 | 1.530 (6) |
| C2—H2B | 0.9300 | C30—C31 | 1.388 (5) |
| C3—C4 | 1.408 (6) | C30—H30A | 0.9300 |
| C3—H3A | 0.9300 | C31—C32 | 1.402 (5) |

| | | | |
|---------------|-----------|---------------|-----------|
| C4—C12 | 1.400 (5) | C31—C36 | 1.498 (5) |
| C4—C5 | 1.429 (6) | C32—C33 | 1.384 (5) |
| C5—C6 | 1.337 (6) | C32—C37 | 1.497 (5) |
| C5—H5A | 0.9300 | C33—H33A | 0.9300 |
| H1WA—O1W—H1WB | 110.5 | C4—C12—C11 | 120.7 (4) |
| C34—O2—H2 | 109.5 | C1—C13—H13A | 109.5 |
| C36—O5—H5 | 109.5 | C1—C13—H13B | 109.5 |
| C37—O8—H8 | 109.5 | H13A—C13—H13B | 109.5 |
| C1—N1—C12 | 123.7 (3) | C1—C13—H13C | 109.5 |
| C1—N1—H1A | 118.2 | H13A—C13—H13C | 109.5 |
| C12—N1—H1A | 118.2 | H13B—C13—H13C | 109.5 |
| C10—N2—C11 | 117.8 (3) | C10—C14—H14A | 109.5 |
| N1—C1—C2 | 117.5 (4) | C10—C14—H14B | 109.5 |
| N1—C1—C13 | 118.7 (4) | H14A—C14—H14B | 109.5 |
| C2—C1—C13 | 123.8 (4) | C10—C14—H14C | 109.5 |
| C3—C2—C1 | 121.0 (4) | H14A—C14—H14C | 109.5 |
| C3—C2—H2B | 119.5 | H14B—C14—H14C | 109.5 |
| C1—C2—H2B | 119.5 | C33—C28—C29 | 118.3 (3) |
| C2—C3—C4 | 121.0 (4) | C33—C28—C34 | 113.5 (3) |
| C2—C3—H3A | 119.5 | C29—C28—C34 | 128.0 (3) |
| C4—C3—H3A | 119.5 | C30—C29—C28 | 118.0 (3) |
| C12—C4—C3 | 117.3 (4) | C30—C29—C35 | 113.0 (3) |
| C12—C4—C5 | 119.2 (4) | C28—C29—C35 | 129.0 (3) |
| C3—C4—C5 | 123.6 (4) | C31—C30—C29 | 122.7 (3) |
| C6—C5—C4 | 120.3 (3) | C31—C30—H30A | 118.6 |
| C6—C5—H5A | 119.8 | C29—C30—H30A | 118.6 |
| C4—C5—H5A | 119.8 | C30—C31—C32 | 119.4 (3) |
| C5—C6—C7 | 122.4 (4) | C30—C31—C36 | 120.7 (3) |
| C5—C6—H6A | 118.8 | C32—C31—C36 | 120.0 (3) |
| C7—C6—H6A | 118.8 | C33—C32—C31 | 117.8 (3) |
| C8—C7—C11 | 116.3 (3) | C33—C32—C37 | 118.4 (3) |
| C8—C7—C6 | 124.7 (4) | C31—C32—C37 | 123.7 (3) |
| C11—C7—C6 | 119.0 (4) | C32—C33—C28 | 123.9 (3) |
| C9—C8—C7 | 119.8 (4) | C32—C33—H33A | 118.1 |
| C9—C8—H8A | 120.1 | C28—C33—H33A | 118.1 |
| C7—C8—H8A | 120.1 | O1—C34—O2 | 120.0 (3) |
| C8—C9—C10 | 120.4 (4) | O1—C34—C28 | 119.6 (3) |
| C8—C9—H9A | 119.8 | O2—C34—C28 | 120.4 (3) |
| C10—C9—H9A | 119.8 | O4—C35—O3 | 122.7 (4) |
| N2—C10—C9 | 121.6 (3) | O4—C35—C29 | 118.5 (3) |
| N2—C10—C14 | 117.6 (3) | O3—C35—C29 | 118.7 (3) |
| C9—C10—C14 | 120.8 (3) | O6—C36—O5 | 123.0 (3) |
| N2—C11—C7 | 124.1 (3) | O6—C36—C31 | 123.4 (3) |
| N2—C11—C12 | 117.6 (3) | O5—C36—C31 | 113.6 (3) |
| C7—C11—C12 | 118.4 (3) | O7—C37—O8 | 120.2 (4) |
| N1—C12—C4 | 119.6 (3) | O7—C37—C32 | 123.1 (4) |
| N1—C12—C11 | 119.8 (3) | O8—C37—C32 | 116.3 (4) |

| | | | |
|----------------|------------|-----------------|------------|
| C12—N1—C1—C2 | -0.2 (6) | C7—C11—C12—C4 | 2.5 (6) |
| C12—N1—C1—C13 | -179.6 (4) | C33—C28—C29—C30 | 0.1 (6) |
| N1—C1—C2—C3 | 0.2 (7) | C34—C28—C29—C30 | -175.6 (4) |
| C13—C1—C2—C3 | 179.6 (4) | C33—C28—C29—C35 | -179.5 (4) |
| C1—C2—C3—C4 | -0.2 (7) | C34—C28—C29—C35 | 4.8 (7) |
| C2—C3—C4—C12 | 0.1 (6) | C28—C29—C30—C31 | 0.0 (6) |
| C2—C3—C4—C5 | -179.2 (4) | C35—C29—C30—C31 | 179.7 (4) |
| C12—C4—C5—C6 | -1.6 (6) | C29—C30—C31—C32 | 0.0 (6) |
| C3—C4—C5—C6 | 177.7 (4) | C29—C30—C31—C36 | 178.6 (4) |
| C4—C5—C6—C7 | 1.7 (7) | C30—C31—C32—C33 | -0.1 (6) |
| C5—C6—C7—C8 | 179.6 (4) | C36—C31—C32—C33 | -178.7 (4) |
| C5—C6—C7—C11 | 0.4 (6) | C30—C31—C32—C37 | 176.7 (4) |
| C11—C7—C8—C9 | 1.9 (6) | C36—C31—C32—C37 | -2.0 (6) |
| C6—C7—C8—C9 | -177.3 (4) | C31—C32—C33—C28 | 0.2 (6) |
| C7—C8—C9—C10 | -1.1 (6) | C37—C32—C33—C28 | -176.7 (4) |
| C11—N2—C10—C9 | 0.7 (6) | C29—C28—C33—C32 | -0.2 (6) |
| C11—N2—C10—C14 | -178.3 (3) | C34—C28—C33—C32 | 176.1 (4) |
| C8—C9—C10—N2 | -0.3 (6) | C33—C28—C34—O1 | -8.9 (6) |
| C8—C9—C10—C14 | 178.7 (4) | C29—C28—C34—O1 | 167.0 (4) |
| C10—N2—C11—C7 | 0.3 (6) | C33—C28—C34—O2 | 170.5 (4) |
| C10—N2—C11—C12 | -179.6 (3) | C29—C28—C34—O2 | -13.6 (7) |
| C8—C7—C11—N2 | -1.6 (6) | C30—C29—C35—O4 | 8.2 (5) |
| C6—C7—C11—N2 | 177.7 (3) | C28—C29—C35—O4 | -172.2 (4) |
| C8—C7—C11—C12 | 178.3 (3) | C30—C29—C35—O3 | -168.0 (3) |
| C6—C7—C11—C12 | -2.5 (6) | C28—C29—C35—O3 | 11.6 (6) |
| C1—N1—C12—C4 | 0.1 (6) | C30—C31—C36—O6 | 175.9 (5) |
| C1—N1—C12—C11 | 180.0 (3) | C32—C31—C36—O6 | -5.4 (7) |
| C3—C4—C12—N1 | -0.1 (6) | C30—C31—C36—O5 | -3.5 (6) |
| C5—C4—C12—N1 | 179.3 (4) | C32—C31—C36—O5 | 175.2 (4) |
| C3—C4—C12—C11 | -179.9 (4) | C33—C32—C37—O7 | -77.6 (5) |
| C5—C4—C12—C11 | -0.6 (6) | C31—C32—C37—O7 | 105.7 (5) |
| N2—C11—C12—N1 | 2.6 (5) | C33—C32—C37—O8 | 95.8 (4) |
| C7—C11—C12—N1 | -177.3 (3) | C31—C32—C37—O8 | -81.0 (5) |
| N2—C11—C12—C4 | -177.6 (3) | | |

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...O3 | 0.82 | 1.58 | 2.395 (4) | 171 |
| O5—H5...O1 ⁱ | 0.82 | 1.86 | 2.671 (3) | 172 |
| O8—H8...O3 ⁱⁱ | 0.82 | 1.82 | 2.645 (4) | 178 |
| N1—H1A...O1W ⁱⁱⁱ | 0.86 | 1.92 | 2.738 (4) | 160 |
| O1W—H1WA...O4 ⁱⁱ | 0.82 | 1.92 | 2.735 (4) | 171 |
| O1W—H1WB...O7 ^{iv} | 0.82 | 2.11 | 2.873 (4) | 155 |

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