



# Crystal structure of 2-hydroxy-*N*-(2-hydroxyethyl)-*N*-{2-hydroxy-3-[(*E*)-*N*-hydroxyethanimidoyl]-5-methylbenzyl}-ethanaminium acetate monohydrate

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Received 8 January 2015; accepted 4 February 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

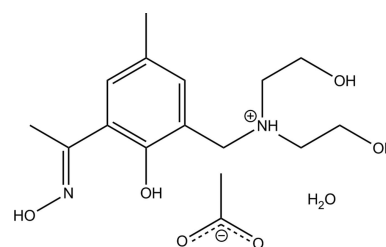
The structure of the title hydrated molecular salt,  $C_{14}H_{23}N_2O_4^+ \cdot C_2H_3O_2^- \cdot H_2O$ , was determined as part of a wider study on the use of the molecule as a polydentate ligand in the synthesis of  $Mn^{III}$  clusters with magnetic properties. The cation features intramolecular  $O-H \cdots N$  and  $N-H \cdots O$  hydrogen-bond interactions. The crystal structure features a range of intermolecular hydrogen-bonding interactions, principally  $O-H \cdots O$  interactions between all three species in the asymmetric unit. An  $R_4^2(8)$  graph-set hydrogen-bonding motif between the anion and water molecules serves as a unit which links to the cation *via* the diethanolamine group. Each O atom of the acetate anion accepts two hydrogen bonds.

**Keywords:** crystal structure; hydrogen bonding; hydrate; organic salt; magnetism.

**CCDC reference:** 1047385

## 1. Related literature

For background literature on Mn-containing single molecule magnets, see: Inglis *et al.* (2012); Milios *et al.* (2007); Tasio-poulos & Perlepes (2008). For examples of the use of 3-[[bis(2-hydroxyethyl)amino]methyl]-2-hydroxy-5-methylbenzaldehyde in the synthesis of magnetic Mn cluster compounds, see: Sanz *et al.* (2014*a,b*) – molecular wheels; Frost *et al.* (2014) – tetrahedron cage. For examples of other magnetic oxime-containing clusters, see: Vlahopoulou *et al.* (2009); Stamatatos *et al.* (2007). For a review of pyridyl–oxime coordination chemistry, see: Milios *et al.* (2006). For the synthesis of 3-[[bis(2-hydroxyethyl)amino]methyl]-2-hydroxy-5-methylbenzaldehyde, see: Wang *et al.* (2006).



## 2. Experimental

### 2.1. Crystal data

$C_{14}H_{23}N_2O_4^+ \cdot C_2H_3O_2^- \cdot H_2O$   
 $M_r = 360.40$   
 Monoclinic,  $P2_1/c$   
 $a = 14.4338$  (5) Å  
 $b = 10.4786$  (3) Å  
 $c = 12.4045$  (4) Å  
 $\beta = 101.593$  (3)°

$V = 1837.86$  (10) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 120$  K  
 $0.48 \times 0.38 \times 0.18$  mm

### 2.2. Data collection

Agilent SuperNova diffractometer  
 Absorption correction: gaussian  
 (*CrysAlis PRO*; Agilent, 2014)  
 $T_{min} = 0.942$ ,  $T_{max} = 0.975$

38067 measured reflections  
 5542 independent reflections  
 4362 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.054$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.129$   
 $S = 1.09$   
 5542 reflections

338 parameters  
 All H-atom parameters refined  
 $\Delta\rho_{max} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.24$  e Å<sup>-3</sup>

**Table 1**  
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> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1 $\cdots$ N1                | 0.85 (2)    | 1.78 (2)            | 2.5368 (16)                | 148 (2)                       |
| O2—H2 $\cdots$ O5                | 0.91 (2)    | 1.71 (2)            | 2.5985 (16)                | 165 (2)                       |
| O3—H3 $\cdots$ O5 <sup>i</sup>   | 0.82 (3)    | 1.82 (3)            | 2.6335 (17)                | 171 (3)                       |
| O4—H4 $\cdots$ O7                | 0.85 (2)    | 1.84 (2)            | 2.6875 (19)                | 176 (2)                       |
| N2—H2A $\cdots$ O1               | 0.903 (19)  | 2.168 (18)          | 2.8121 (16)                | 127.6 (15)                    |
| O7—H7A $\cdots$ O6               | 0.79 (3)    | 2.07 (3)            | 2.823 (2)                  | 159 (3)                       |
| O7—H7B $\cdots$ O6 <sup>ii</sup> | 0.89 (3)    | 1.86 (3)            | 2.738 (2)                  | 169 (2)                       |

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

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

## Acknowledgements

We thank The University of Edinburgh for funding the diffractometer purchase.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7350).

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## supporting information

*Acta Cryst.* (2015). E71, o186–o187 [doi:10.1107/S2056989015002418]

## Crystal structure of 2-hydroxy-*N*-(2-hydroxyethyl)-*N*-{2-hydroxy-3-[(*E*)-*N*-hydroxyethanimidoyl]-5-methylbenzyl}ethanaminium acetate monohydrate

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### S1. Chemical context

The structure of the title hydrated salt was determined as part of a wider study on the synthesis of polymetallic compounds with potentially interesting magnetic properties. The phenolic oximes are a ligand family which have had enormous success in the construction of Mn cluster compounds that behave as single molecule magnets (Milios *et al.*, 2007; Inglis *et al.*, 2012). These ligand types tend to form systems based on the  $[\text{Mn}_3\text{O}(\text{L})_3]^+$  (L = salicylaldoxime) building block (Vlahopoulou *et al.*, 2009; Stamatatos *et al.*, 2007; Milios *et al.*, 2006). An additional functional group was introduced onto the aromatic framework of the ligand in an attempt to disrupt the formation of clusters based on this motif and to see if higher nuclearity compounds based on phenolic oximes could be isolated. A diethanolamine functional group was the obvious choice given that this has an excellent track record of making magnetically interesting Mn clusters in its own right (Tasiopoulos & Perlepes, 2008). For examples of the use of the  $\text{H}_4\text{L}$  in the synthesis of magnetic materials, see Frost *et al.* (2014) and Sanz *et al.* (2014a, 2014b).

### S2. Structural commentary

A check of the molecular geometry with Mogul showed all geometric parameters to be unexceptional. A mean plane fitted through atoms O1, O2, N1 and C1 to C10 (i.e. all ring atoms plus the oxime and hydroxyl groups) has an rms deviation of 0.029 Å.

### S3. Supramolecular features

The crystal structure features extensive hydrogen bonding, principally O–H $\cdots$ O interactions involving all species in the asymmetric unit. Intramolecular interactions within the cation are, perhaps, less important but serve to support the overall structure by locking the cation conformation. The N2–H2A $\cdots$ O1 interaction in particular is probably quite weak. The  $R_4^2(8)$  graph set motif between the anion and water molecules serves as an important unit which links to the cation via the hydroxyethane groups to propagate the three-dimensional structure. Hydrogen bonding information is summarised in Table 2.

### S4. Synthesis and crystallization

#### Experimental Procedures

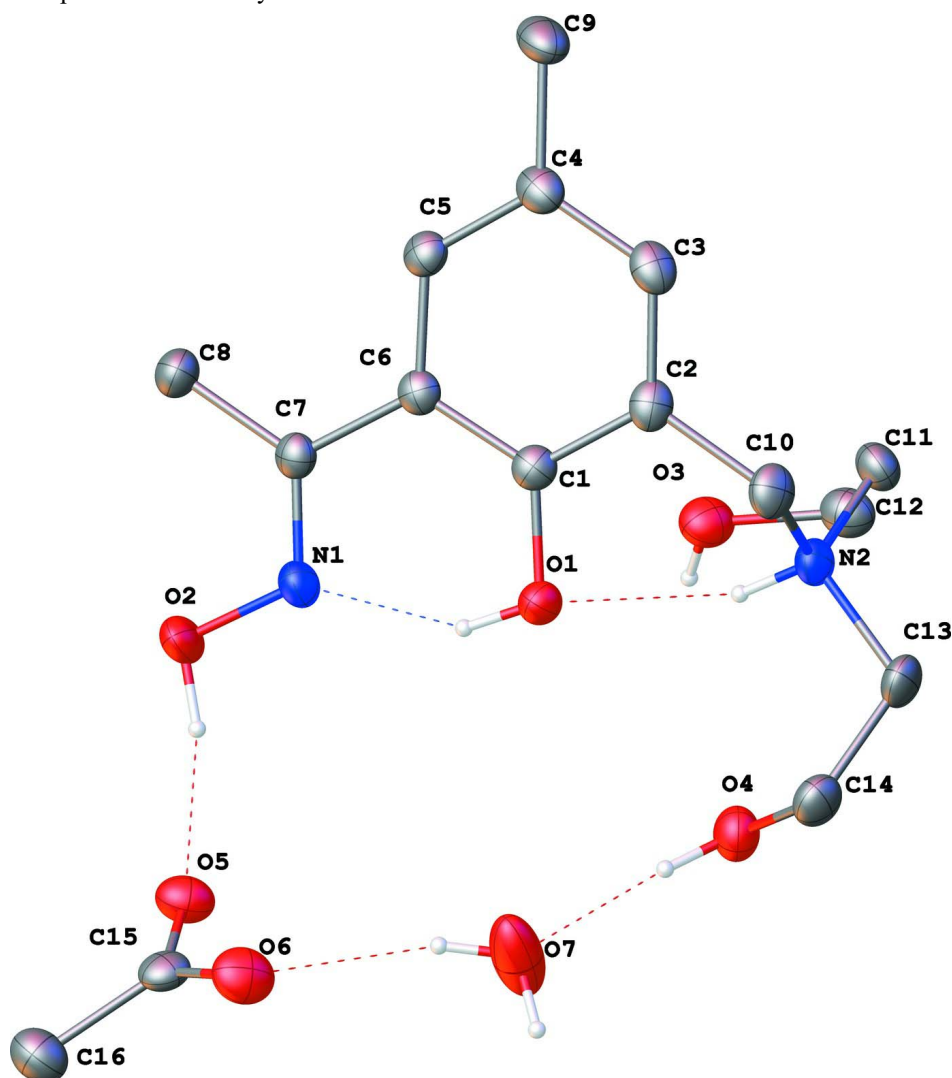
$^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were recorded on a nav 500 MHz spectrometer. 3-((Bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylbenzaldehyde was prepared according to a published procedure (Wang *et al.*, 2006). Solvents and reagents were used as received from commercial suppliers.

**Synthesis of 3-[[Bis(2-hydroxyethyl)amino]methyl]-2-hydroxy-5-methylsalicylaldoxime ( $\text{H}_4\text{L}$ )**

3-{[Bis(2-hydroxyethyl)amino]methyl}-2-hydroxy-5-methylbenzaldehyde (10.8 g, 40 mmol), hydroxylamine hydrochloride (3.5 g, 50 mmol) and sodium acetate (4.14 g, 50 mmol) were dissolved in 500 mL of ethanol. The mixture was refluxed under N<sub>2</sub> for 4 h. A white precipitate was filtered off from the warm ethanol solution. The solvent was evaporated to dryness, a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> added and the sample stored at -10°C for 24 hours. Clear block shaped crystals grew and were collected after filtration (10.16 g, 90%). <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  7.12 (bs, 1H), 7.05 (bs, 1H), 3.60 (s, 2H), 3.54 (t,  $J=6.2$  Hz, 4H), 2.53 (t,  $J=6.2$  Hz, 4H), 2.23 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C NMR (500 MHz, DMSO):  $\delta$  157.28 (1C, C<sub>ar</sub>OH), 153.86 (1C, CNOH), 131.34 (1C, CH), 127.61 (1C, CH), 126.99 (1C, C), 124.34 (1C, C), 121.01 (1C, C), 59.14 (2C, CH<sub>2</sub>), 56.51 (2C, CH<sub>2</sub>), 54.78 (1C, CH<sub>2</sub>), 21.69 (1C, CH<sub>3</sub>), 12.73 (1C, CH<sub>3</sub>).

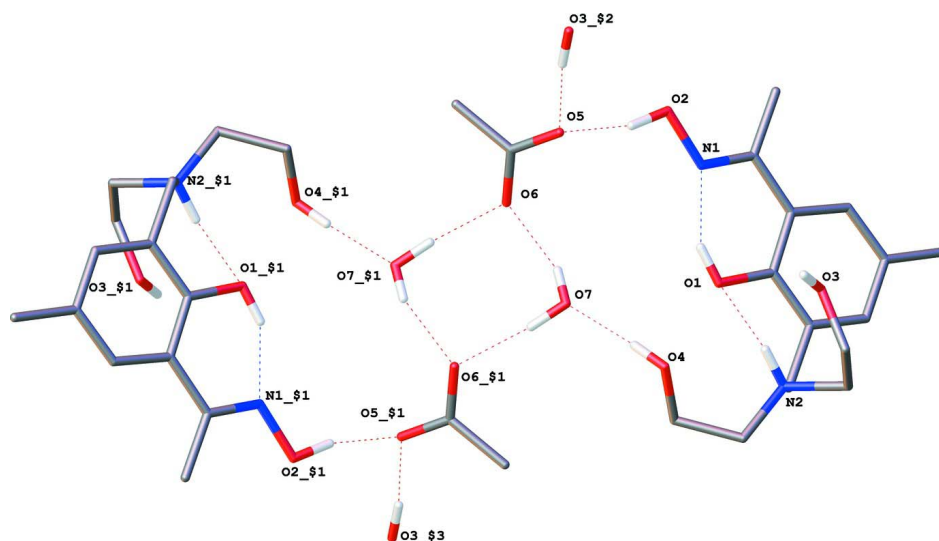
## S5. Refinement

Crystal data, data collection and structure refinement details are summarised in Table 1. All H atoms were located in a difference Fourier map and refined freely.



**Figure 1**

The asymmetric unit of H<sub>4</sub>L. Displacement ellipsoids are at the 50% probability level and C-bound H atoms have been omitted.

**Figure 2**

Hydrogen-bonding interactions, indicated by dashed lines, in the crystal structure of  $H_4L$ . Symmetry operations for equivalent atoms: \$1, 1 - x, -y, 2 - z\$; \$2, x, 1/2 - y, 1/2 + z\$; \$3, 1 - x, -1/2 + y, 3/2 - z\$.

**2-Hydroxy-*N*-(2-hydroxyethyl)-*N*-{2-hydroxy-3-[(*E*)-*N*-hydroxyethanimidoyl]-5-methylbenzyl}ethanaminium acetate monohydrate**

*Crystal data*

$C_{14}H_{23}N_2O_4^+ \cdot C_2H_3O_2^- \cdot H_2O$

$M_r = 360.40$

Monoclinic,  $P2_1/c$

$a = 14.4338$  (5) Å

$b = 10.4786$  (3) Å

$c = 12.4045$  (4) Å

$\beta = 101.593$  (3)°

$V = 1837.86$  (10) Å<sup>3</sup>

$Z = 4$

$F(000) = 776$

$D_x = 1.303$  Mg m<sup>-3</sup>

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

Cell parameters from 10187 reflections

$\theta = 3.5\text{--}30.2^\circ$

$\mu = 0.10$  mm<sup>-1</sup>

$T = 120$  K

Block, colourless

$0.48 \times 0.38 \times 0.18$  mm

*Data collection*

Agilent SuperNova

diffractometer

Radiation source: SuperNova (Mo) X-ray

Source

Mirror monochromator

Detector resolution: 5.1574 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: gaussian

(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.942$ ,  $T_{\max} = 0.975$

38067 measured reflections

5542 independent reflections

4362 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 31.1^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -20 \rightarrow 20$

$k = -15 \rightarrow 13$

$l = -18 \rightarrow 17$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.129$

$S = 1.09$

5542 reflections

338 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.9291P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

### 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.** All H atoms were located in a difference Fourier map and refined freely.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|      | <i>x</i>      | <i>y</i>      | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|---------------|--------------|----------------------------------|
| O1   | 0.25286 (7)   | −0.10957 (10) | 0.65849 (9)  | 0.0229 (2)                       |
| H1   | 0.2395 (15)   | −0.050 (2)    | 0.6990 (18)  | 0.046 (6)*                       |
| O2   | 0.14106 (9)   | 0.14279 (11)  | 0.81376 (9)  | 0.0320 (3)                       |
| H2   | 0.2011 (17)   | 0.160 (2)     | 0.8484 (19)  | 0.054 (7)*                       |
| O3   | 0.24215 (8)   | 0.03539 (12)  | 0.40801 (10) | 0.0304 (3)                       |
| H3   | 0.2659 (18)   | 0.107 (3)     | 0.418 (2)    | 0.060 (7)*                       |
| O4   | 0.45674 (8)   | −0.04092 (11) | 0.61916 (10) | 0.0300 (3)                       |
| H4   | 0.4552 (16)   | −0.026 (2)    | 0.686 (2)    | 0.055 (7)*                       |
| N1   | 0.15152 (9)   | 0.03976 (12)  | 0.74689 (10) | 0.0232 (3)                       |
| N2   | 0.32127 (9)   | −0.19342 (12) | 0.47375 (10) | 0.0220 (3)                       |
| H2A  | 0.3117 (13)   | −0.1223 (18)  | 0.5112 (15)  | 0.028 (5)*                       |
| C1   | 0.16920 (10)  | −0.16143 (13) | 0.60648 (11) | 0.0202 (3)                       |
| C2   | 0.17518 (10)  | −0.26194 (13) | 0.53438 (12) | 0.0223 (3)                       |
| C3   | 0.09294 (11)  | −0.32024 (14) | 0.47871 (12) | 0.0246 (3)                       |
| H3A  | 0.0993 (13)   | −0.3890 (18)  | 0.4276 (15)  | 0.029 (5)*                       |
| C4   | 0.00394 (11)  | −0.27997 (14) | 0.49290 (12) | 0.0243 (3)                       |
| C5   | −0.00027 (10) | −0.17826 (14) | 0.56389 (11) | 0.0213 (3)                       |
| H5   | −0.0609 (13)  | −0.1492 (17)  | 0.5733 (14)  | 0.024 (4)*                       |
| C6   | 0.08079 (10)  | −0.11679 (13) | 0.62184 (11) | 0.0192 (3)                       |
| C7   | 0.07274 (10)  | −0.00789 (14) | 0.69504 (11) | 0.0203 (3)                       |
| C8   | −0.02208 (11) | 0.04239 (17)  | 0.70539 (14) | 0.0264 (3)                       |
| H8A  | −0.0567 (16)  | 0.073 (2)     | 0.638 (2)    | 0.053 (6)*                       |
| H8B  | −0.0153 (17)  | 0.104 (2)     | 0.757 (2)    | 0.058 (7)*                       |
| H8C  | −0.0601 (16)  | −0.026 (2)    | 0.7244 (18)  | 0.052 (6)*                       |
| C9   | −0.08552 (13) | −0.34031 (18) | 0.43012 (14) | 0.0323 (4)                       |
| H9A  | −0.1036 (15)  | −0.305 (2)    | 0.3569 (18)  | 0.042 (6)*                       |
| H9B  | −0.1359 (18)  | −0.334 (2)    | 0.474 (2)    | 0.063 (7)*                       |
| H9C  | −0.0770 (15)  | −0.429 (2)    | 0.4181 (18)  | 0.048 (6)*                       |
| C10  | 0.27174 (11)  | −0.30209 (14) | 0.51927 (14) | 0.0261 (3)                       |
| H10A | 0.2691 (13)   | −0.3701 (19)  | 0.4675 (16)  | 0.032 (5)*                       |
| H10B | 0.3144 (13)   | −0.3244 (17)  | 0.5908 (15)  | 0.027 (5)*                       |
| C11  | 0.27852 (12)  | −0.16896 (15) | 0.35473 (12) | 0.0259 (3)                       |
| H11A | 0.2117 (13)   | −0.1940 (17)  | 0.3425 (14)  | 0.024 (4)*                       |
| H11B | 0.3108 (13)   | −0.2206 (19)  | 0.3119 (15)  | 0.032 (5)*                       |
| C12  | 0.28636 (12)  | −0.02870 (16) | 0.33149 (13) | 0.0294 (3)                       |

|      |              |               |              |             |
|------|--------------|---------------|--------------|-------------|
| H12A | 0.3503 (14)  | −0.0019 (18)  | 0.3386 (15)  | 0.032 (5)*  |
| H12B | 0.2514 (13)  | −0.0128 (18)  | 0.2536 (15)  | 0.030 (5)*  |
| C13  | 0.42648 (11) | −0.21255 (17) | 0.49313 (14) | 0.0288 (3)  |
| H13A | 0.4494 (12)  | −0.1530 (17)  | 0.4413 (14)  | 0.025 (4)*  |
| H13B | 0.4385 (12)  | −0.3021 (18)  | 0.4792 (14)  | 0.027 (4)*  |
| C14  | 0.47242 (12) | −0.17376 (17) | 0.60884 (14) | 0.0298 (3)  |
| H14A | 0.5399 (14)  | −0.1927 (18)  | 0.6200 (15)  | 0.034 (5)*  |
| H14B | 0.4445 (13)  | −0.2225 (18)  | 0.6635 (15)  | 0.030 (5)*  |
| O5   | 0.30047 (8)  | 0.22604 (11)  | 0.92796 (9)  | 0.0297 (3)  |
| O6   | 0.38120 (9)  | 0.06607 (11)  | 1.01687 (10) | 0.0349 (3)  |
| C15  | 0.34399 (10) | 0.17389 (14)  | 1.01535 (13) | 0.0242 (3)  |
| C16  | 0.35169 (15) | 0.24691 (19)  | 1.12192 (15) | 0.0347 (4)  |
| H16A | 0.409 (2)    | 0.234 (3)     | 1.167 (3)    | 0.098 (11)* |
| H16B | 0.348 (2)    | 0.337 (3)     | 1.110 (3)    | 0.101 (11)* |
| H16C | 0.307 (2)    | 0.221 (3)     | 1.162 (3)    | 0.108 (12)* |
| O7   | 0.46060 (14) | 0.00383 (17)  | 0.83335 (12) | 0.0569 (5)  |
| H7A  | 0.4274 (18)  | 0.028 (3)     | 0.873 (2)    | 0.059 (8)*  |
| H7B  | 0.5160 (19)  | −0.016 (3)    | 0.875 (2)    | 0.064 (8)*  |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|-------------|-------------|------------|-------------|-------------|-------------|
| O1  | 0.0198 (5)  | 0.0238 (5)  | 0.0247 (5) | 0.0018 (4)  | 0.0037 (4)  | −0.0027 (4) |
| O2  | 0.0276 (6)  | 0.0354 (6)  | 0.0320 (6) | 0.0025 (5)  | 0.0035 (5)  | −0.0167 (5) |
| O3  | 0.0300 (6)  | 0.0243 (6)  | 0.0361 (6) | −0.0018 (5) | 0.0048 (5)  | −0.0022 (5) |
| O4  | 0.0306 (6)  | 0.0328 (6)  | 0.0282 (6) | 0.0025 (5)  | 0.0099 (5)  | −0.0019 (5) |
| N1  | 0.0251 (6)  | 0.0229 (6)  | 0.0216 (6) | 0.0016 (5)  | 0.0051 (5)  | −0.0044 (5) |
| N2  | 0.0225 (6)  | 0.0208 (6)  | 0.0233 (6) | 0.0035 (5)  | 0.0062 (5)  | −0.0030 (5) |
| C1  | 0.0223 (7)  | 0.0177 (6)  | 0.0208 (6) | 0.0002 (5)  | 0.0046 (5)  | 0.0031 (5)  |
| C2  | 0.0268 (7)  | 0.0167 (6)  | 0.0251 (7) | 0.0020 (5)  | 0.0096 (6)  | 0.0036 (5)  |
| C3  | 0.0343 (8)  | 0.0166 (6)  | 0.0247 (7) | −0.0023 (6) | 0.0098 (6)  | 0.0001 (5)  |
| C4  | 0.0291 (8)  | 0.0232 (7)  | 0.0218 (6) | −0.0063 (6) | 0.0077 (6)  | 0.0005 (5)  |
| C5  | 0.0214 (7)  | 0.0226 (7)  | 0.0208 (6) | −0.0016 (5) | 0.0070 (5)  | 0.0025 (5)  |
| C6  | 0.0223 (7)  | 0.0180 (6)  | 0.0178 (6) | −0.0002 (5) | 0.0053 (5)  | 0.0029 (5)  |
| C7  | 0.0223 (7)  | 0.0218 (7)  | 0.0177 (6) | 0.0008 (5)  | 0.0061 (5)  | 0.0017 (5)  |
| C8  | 0.0227 (8)  | 0.0304 (8)  | 0.0271 (7) | 0.0018 (6)  | 0.0075 (6)  | −0.0024 (6) |
| C9  | 0.0333 (9)  | 0.0343 (9)  | 0.0303 (8) | −0.0124 (7) | 0.0085 (7)  | −0.0093 (7) |
| C10 | 0.0301 (8)  | 0.0185 (7)  | 0.0312 (8) | 0.0048 (6)  | 0.0097 (6)  | 0.0005 (6)  |
| C11 | 0.0294 (8)  | 0.0282 (8)  | 0.0204 (6) | −0.0018 (6) | 0.0057 (6)  | −0.0049 (6) |
| C12 | 0.0313 (9)  | 0.0310 (8)  | 0.0251 (7) | −0.0038 (6) | 0.0039 (6)  | 0.0016 (6)  |
| C13 | 0.0217 (8)  | 0.0337 (9)  | 0.0326 (8) | 0.0081 (6)  | 0.0091 (6)  | −0.0046 (7) |
| C14 | 0.0224 (8)  | 0.0337 (9)  | 0.0331 (8) | 0.0074 (6)  | 0.0050 (6)  | −0.0006 (7) |
| O5  | 0.0302 (6)  | 0.0252 (6)  | 0.0310 (6) | −0.0027 (4) | −0.0003 (5) | 0.0003 (4)  |
| O6  | 0.0394 (7)  | 0.0216 (6)  | 0.0417 (7) | 0.0006 (5)  | 0.0032 (5)  | −0.0002 (5) |
| C15 | 0.0192 (7)  | 0.0219 (7)  | 0.0311 (7) | −0.0064 (5) | 0.0043 (6)  | −0.0005 (6) |
| C16 | 0.0391 (10) | 0.0332 (9)  | 0.0309 (8) | −0.0034 (7) | 0.0044 (7)  | −0.0042 (7) |
| O7  | 0.0679 (11) | 0.0706 (11) | 0.0285 (7) | 0.0369 (9)  | 0.0011 (7)  | −0.0062 (7) |

*Geometric parameters (Å, °)*

|            |             |               |             |
|------------|-------------|---------------|-------------|
| O1—H1      | 0.85 (2)    | C8—H8B        | 0.91 (3)    |
| O1—C1      | 1.3625 (17) | C8—H8C        | 0.96 (2)    |
| O2—H2      | 0.91 (2)    | C9—H9A        | 0.97 (2)    |
| O2—N1      | 1.3880 (16) | C9—H9B        | 0.99 (3)    |
| O3—H3      | 0.82 (3)    | C9—H9C        | 0.96 (2)    |
| O3—C12     | 1.415 (2)   | C10—H10A      | 0.95 (2)    |
| O4—H4      | 0.85 (2)    | C10—H10B      | 1.001 (18)  |
| O4—C14     | 1.420 (2)   | C11—H11A      | 0.982 (18)  |
| N1—C7      | 1.2891 (19) | C11—H11B      | 0.94 (2)    |
| N2—H2A     | 0.903 (19)  | C11—C12       | 1.506 (2)   |
| N2—C10     | 1.513 (2)   | C12—H12A      | 0.952 (19)  |
| N2—C11     | 1.5034 (19) | C12—H12B      | 1.009 (18)  |
| N2—C13     | 1.503 (2)   | C13—H13A      | 0.999 (18)  |
| C1—C2      | 1.396 (2)   | C13—H13B      | 0.976 (19)  |
| C1—C6      | 1.408 (2)   | C13—C14       | 1.511 (2)   |
| C2—C3      | 1.389 (2)   | C14—H14A      | 0.98 (2)    |
| C2—C10     | 1.503 (2)   | C14—H14B      | 0.996 (19)  |
| C3—H3A     | 0.976 (19)  | O5—C15        | 1.2628 (18) |
| C3—C4      | 1.396 (2)   | O6—C15        | 1.2495 (19) |
| C4—C5      | 1.392 (2)   | C15—C16       | 1.512 (2)   |
| C4—C9      | 1.506 (2)   | C16—H16A      | 0.91 (3)    |
| C5—H5      | 0.955 (18)  | C16—H16B      | 0.96 (4)    |
| C5—C6      | 1.401 (2)   | C16—H16C      | 0.92 (4)    |
| C6—C7      | 1.4773 (19) | O7—H7A        | 0.79 (3)    |
| C7—C8      | 1.496 (2)   | O7—H7B        | 0.89 (3)    |
| C8—H8A     | 0.95 (2)    |               |             |
| C1—O1—H1   | 106.8 (15)  | H9A—C9—H9C    | 104.1 (18)  |
| N1—O2—H2   | 103.4 (15)  | H9B—C9—H9C    | 106 (2)     |
| C12—O3—H3  | 107.3 (18)  | N2—C10—H10A   | 105.6 (11)  |
| C14—O4—H4  | 107.4 (17)  | N2—C10—H10B   | 104.7 (10)  |
| C7—N1—O2   | 114.11 (12) | C2—C10—N2     | 110.81 (12) |
| C10—N2—H2A | 107.2 (12)  | C2—C10—H10A   | 112.3 (11)  |
| C11—N2—H2A | 106.8 (11)  | C2—C10—H10B   | 112.1 (10)  |
| C11—N2—C10 | 111.31 (12) | H10A—C10—H10B | 110.8 (15)  |
| C13—N2—H2A | 106.4 (11)  | N2—C11—H11A   | 107.6 (10)  |
| C13—N2—C10 | 112.21 (12) | N2—C11—H11B   | 107.6 (11)  |
| C13—N2—C11 | 112.46 (12) | N2—C11—C12    | 108.81 (12) |
| O1—C1—C2   | 116.19 (13) | H11A—C11—H11B | 109.9 (15)  |
| O1—C1—C6   | 123.00 (13) | C12—C11—H11A  | 109.9 (10)  |
| C2—C1—C6   | 120.80 (13) | C12—C11—H11B  | 112.7 (12)  |
| C1—C2—C10  | 118.00 (13) | O3—C12—C11    | 105.86 (13) |
| C3—C2—C1   | 119.59 (14) | O3—C12—H12A   | 111.0 (11)  |
| C3—C2—C10  | 122.41 (13) | O3—C12—H12B   | 111.0 (10)  |
| C2—C3—H3A  | 117.7 (11)  | C11—C12—H12A  | 112.2 (12)  |
| C2—C3—C4   | 121.35 (14) | C11—C12—H12B  | 107.6 (11)  |

|               |              |                |              |
|---------------|--------------|----------------|--------------|
| C4—C3—H3A     | 120.9 (11)   | H12A—C12—H12B  | 109.2 (15)   |
| C3—C4—C9      | 121.51 (14)  | N2—C13—H13A    | 105.6 (10)   |
| C5—C4—C3      | 118.00 (14)  | N2—C13—H13B    | 108.1 (10)   |
| C5—C4—C9      | 120.44 (15)  | N2—C13—C14     | 110.65 (12)  |
| C4—C5—H5      | 118.6 (11)   | H13A—C13—H13B  | 113.1 (15)   |
| C4—C5—C6      | 122.59 (14)  | C14—C13—H13A   | 107.7 (10)   |
| C6—C5—H5      | 118.8 (11)   | C14—C13—H13B   | 111.5 (10)   |
| C1—C6—C7      | 121.69 (13)  | O4—C14—C13     | 107.57 (13)  |
| C5—C6—C1      | 117.66 (13)  | O4—C14—H14A    | 111.1 (12)   |
| C5—C6—C7      | 120.65 (13)  | O4—C14—H14B    | 110.4 (11)   |
| N1—C7—C6      | 115.82 (13)  | C13—C14—H14A   | 108.3 (11)   |
| N1—C7—C8      | 123.45 (13)  | C13—C14—H14B   | 110.4 (11)   |
| C6—C7—C8      | 120.73 (13)  | H14A—C14—H14B  | 109.1 (15)   |
| C7—C8—H8A     | 112.0 (14)   | O5—C15—C16     | 117.90 (14)  |
| C7—C8—H8B     | 110.1 (15)   | O6—C15—O5      | 122.85 (15)  |
| C7—C8—H8C     | 109.7 (14)   | O6—C15—C16     | 119.25 (15)  |
| H8A—C8—H8B    | 110 (2)      | C15—C16—H16A   | 111 (2)      |
| H8A—C8—H8C    | 104.4 (19)   | C15—C16—H16B   | 112 (2)      |
| H8B—C8—H8C    | 110 (2)      | C15—C16—H16C   | 113 (2)      |
| C4—C9—H9A     | 111.6 (13)   | H16A—C16—H16B  | 105 (3)      |
| C4—C9—H9B     | 109.7 (14)   | H16A—C16—H16C  | 106 (3)      |
| C4—C9—H9C     | 111.5 (13)   | H16B—C16—H16C  | 111 (3)      |
| H9A—C9—H9B    | 113.5 (19)   | H7A—O7—H7B     | 107 (2)      |
| O1—C1—C2—C3   | 179.65 (12)  | C3—C2—C10—N2   | 118.43 (15)  |
| O1—C1—C2—C10  | −0.96 (19)   | C3—C4—C5—C6    | −0.8 (2)     |
| O1—C1—C6—C5   | −179.83 (12) | C4—C5—C6—C1    | −0.1 (2)     |
| O1—C1—C6—C7   | 1.0 (2)      | C4—C5—C6—C7    | 179.07 (13)  |
| O2—N1—C7—C6   | 179.25 (11)  | C5—C6—C7—N1    | 178.18 (13)  |
| O2—N1—C7—C8   | −0.1 (2)     | C5—C6—C7—C8    | −2.5 (2)     |
| N2—C11—C12—O3 | −55.59 (16)  | C6—C1—C2—C3    | −1.3 (2)     |
| N2—C13—C14—O4 | −63.57 (17)  | C6—C1—C2—C10   | 178.13 (13)  |
| C1—C2—C3—C4   | 0.3 (2)      | C9—C4—C5—C6    | −178.27 (14) |
| C1—C2—C10—N2  | −60.94 (17)  | C10—N2—C11—C12 | 148.01 (13)  |
| C1—C6—C7—N1   | −2.68 (19)   | C10—N2—C13—C14 | −81.01 (16)  |
| C1—C6—C7—C8   | 176.67 (13)  | C10—C2—C3—C4   | −179.04 (14) |
| C2—C1—C6—C5   | 1.1 (2)      | C11—N2—C10—C2  | −72.47 (15)  |
| C2—C1—C6—C7   | −178.03 (12) | C11—N2—C13—C14 | 152.57 (14)  |
| C2—C3—C4—C5   | 0.7 (2)      | C13—N2—C10—C2  | 160.50 (12)  |
| C2—C3—C4—C9   | 178.13 (14)  | C13—N2—C11—C12 | −85.09 (16)  |

## 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> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1 $\cdots$ N1              | 0.85 (2)    | 1.78 (2)            | 2.5368 (16)                | 148 (2)                       |
| O2—H2 $\cdots$ O5              | 0.91 (2)    | 1.71 (2)            | 2.5985 (16)                | 165 (2)                       |
| O3—H3 $\cdots$ O5 <sup>i</sup> | 0.82 (3)    | 1.82 (3)            | 2.6335 (17)                | 171 (3)                       |
| O4—H4 $\cdots$ O7              | 0.85 (2)    | 1.84 (2)            | 2.6875 (19)                | 176 (2)                       |

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|                           |            |            |             |            |
|---------------------------|------------|------------|-------------|------------|
| N2—H2A···O1               | 0.903 (19) | 2.168 (18) | 2.8121 (16) | 127.6 (15) |
| O7—H7A···O6               | 0.79 (3)   | 2.07 (3)   | 2.823 (2)   | 159 (3)    |
| O7—H7B···O6 <sup>ii</sup> | 0.89 (3)   | 1.86 (3)   | 2.738 (2)   | 169 (2)    |

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