# metal-organic compounds

# 1,4-Diazoniabicyclo[2.2.2]octane hexaaquamagnesium bis(sulfate)

## Wen-Ni Zheng

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In the title compound, $(C_6H_{14}N_2)[Mg(H_2O)_6](SO_4)_2$, the $Mg^{II}$ ion, lying on an inversion center, is coordinated by six water molecules in a slightly distorted octahedral geometry. The 1,4-diazoniabicyclo[2.2.2]octane cation is located about a twofold rotation axis. Intermolecular N—H···O and O—H···O hydrogen bonds link the cations and the anions into a three-dimensional network.

## Related literature

For the properties and applications of amide salt compounds, see: Fu *et al.* (2007, 2008, 2009); Fu & Xiong (2008).
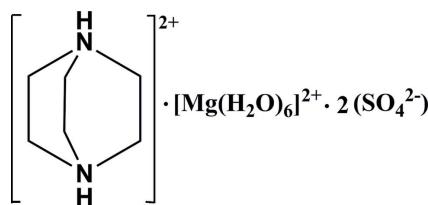


## Experimental

### Crystal data

$(C_6H_{14}N_2)[Mg(H_2O)_6](SO_4)_2$
$M_r = 438.74$
Monoclinic, $C2/c$
$a = 14.968$ (3) Å
$b = 9.1860$ (18) Å
$c = 14.334$ (3) Å
$\beta = 117.12$ (3)°

$V = 1754.2$ (8) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.41$ mm$^{-1}$
$T = 298$ K
$0.40 \times 0.30 \times 0.20$ mm

### Data collection

Rigaku SCXmini CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.89$, $T_{max} = 0.95$

8747 measured reflections
2014 independent reflections
1839 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.169$
$S = 1.26$
2014 reflections

116 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.30$ e Å$^{-3}$
$\Delta\rho_{min} = -1.08$ e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O3$^i$ | 0.91 | 1.87 | 2.734 (3) | 157 |
| O1$W$—H1$WA$···O3$^i$ | 0.85 | 1.90 | 2.751 (3) | 179 |
| O1$W$—H1$WB$···O1$^{ii}$ | 0.85 | 2.01 | 2.835 (3) | 165 |
| O2$W$—H2$WA$···O2 | 0.85 | 2.00 | 2.809 (3) | 158 |
| O2$W$—H2$WB$···O2$^{iii}$ | 0.85 | 1.83 | 2.674 (3) | 173 |
| O3$W$—H3$WA$···O4$^{iv}$ | 0.85 | 1.85 | 2.694 (3) | 170 |
| O3$W$—H3$WB$···O1$^{iii}$ | 0.85 | 1.92 | 2.769 (3) | 177 |

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

Data collection: *CrystalClear* (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: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

## References

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Fu, D.-W., Ge, J.-Z., Dai, J., Ye, H.-Y. & Qu, Z.-R. (2009). *Inorg. Chem. Commun.* **12**, 994–997.
Fu, D.-W., Song, Y.-M., Wang, G.-X., Ye, Q., Xiong, R.-G., Akutagawa, T., Nakamura, T., Chan, P. W. H. & Huang, S. D. (2007). *J. Am. Chem. Soc.* **129**, 5346–5347.
Fu, D.-W. & Xiong, R.-G. (2008). *Dalton Trans.* pp. 3946–3948.
Fu, D.-W., Zhang, W. & Xiong, R.-G. (2008). *Cryst. Growth Des.* **8**, 3461–3464.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

# 1,4-Diazoniabicyclo[2.2.2]octane hexaaquamagnesium bis(sulfate)

## Wen-Ni Zheng

## S1. Comment

Salts of amide have attracted more attention as phase transition dielectric materials for their applications in micro-electronics and memory storage (Fu *et al.*, 2007, 2008, 2009; Fu & Xiong, 2008). With the purpose of obtaining phase transition crystals, the interactions of 1,4-diazabicyclo[2.2.2]octane with various metal ions have been studied and we have elaborated a serie of new materials with this organic molecule. In this paper, we describe the crystal structure of the title compound.

The asymmetric unit is composed of an $SO_4^{2-}$ anion, half 1,4-diazoniabicyclo[2.2.2]octane cation and half $[Mg(H_2O)_6]^{2+}$ cation. (Fig. 1). The $Mg^{II}$ ion, lying on an inversion center, is in a slightly distorted octahedral geometry formed by six O atoms from the water molecules. The $[Mg(H_2O)_6]^{2+}$ cation possesses typical Mg—O bond lengths [2.035 (2)–2.086 (2) Å], while the O—Mg—O bond angles [88.90 (8)–91.86 (9)°] indicating some distortion from a regular octahedron.

In the crystal, the interionic hydrogen bonds are formed by all H atoms of the water molecules and the amine groups with all O atoms of the $SO_4^{2-}$ anion and its symmetric equivalents (Table 1). The complex cations $[Mg(H_2O)_6]^{2+}$ and $SO_4^{2-}$ anions are linked through O—H···O hydrogen bonds into a three-dimensional network, indicating that $SO_4^{2-}$ anion is a good hydrogen-bonding acceptor. In addition, the amino cations are hydrogen bonded to the $SO_4^{2-}$ anions through N—H···O hydrogen bonds, which play an important role in stabilizing the crystal structure (Fig. 2).

## S2. Experimental

Commercial 1,4-diazabicyclo[2.2.2]octane (3 mmol), $H_2SO_4$ (3 mmol) and $MgSO_4$ (3 mmol) were dissolved in water. The solvent was slowly evaporated in air, affording colorless block-shaped crystals of the title compound suitable for X-ray analysis.

The permittivity measurement shows that there is no phase transition within the temperature range from 100 to 400 K, while the permittivity is 10.2 at 1 MHz at room temperature.

## S3. Refinement

H atoms attached to C and N atoms were positioned geometrically and treated as riding, with C—H = 0.97 and N—H = 0.91 Å and with $U_{iso}(H) = 1.2U_{eq}(C, N)$. H atoms of water molecules were located in difference Fourier maps and refined as riding atoms, with O—H = 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The highest residual electron density was found at 1.18 Å from H1B atom and the deepest hole at 1.42 Å from C2 atom.
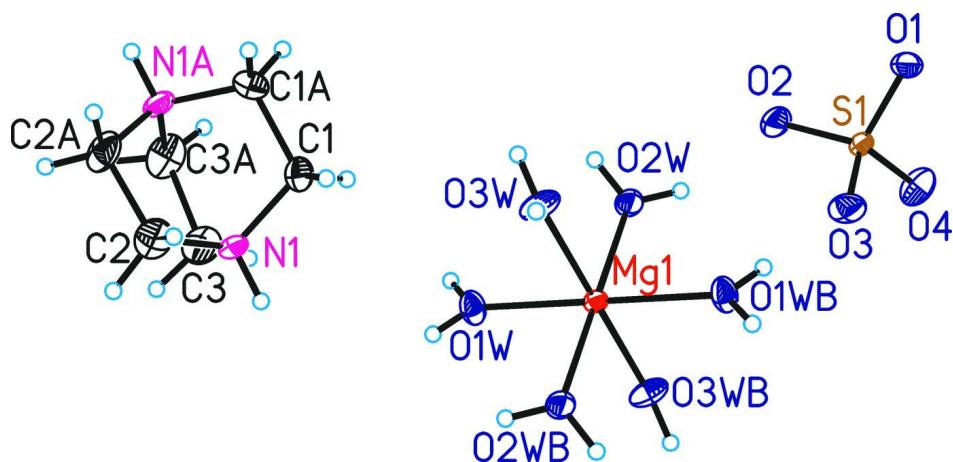
**Figure 1**

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (A) -x, y, 0.5-z; (B) 0.5-x, 0.5-y, -z.]
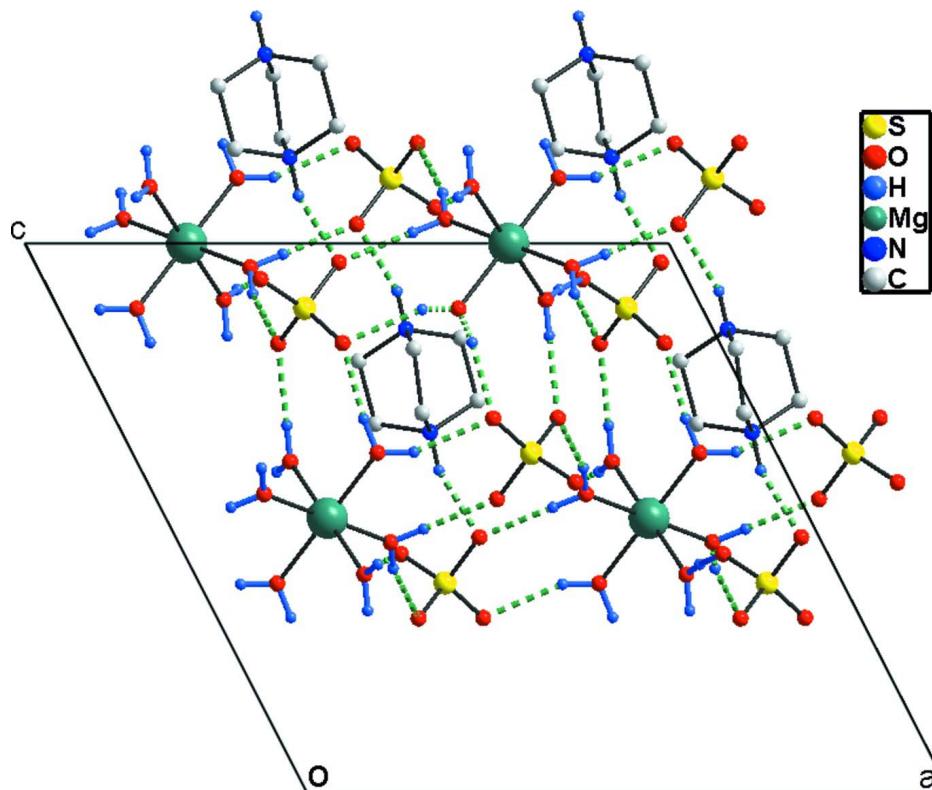


**Figure 2**

The crystal packing of the title compound, showing the three-dimensional hydrogen-bonded network. H atoms not involved in hydrogen bonds (dashed lines) have been omitted for clarity.

**1,4-Diazoniabicyclo[2.2.2]octane hexaaquamagnesium bis(sulfate)**

*Crystal data*
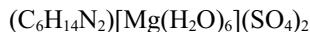
| | |
|---|---|
| $(C_6H_{14}N_2)[Mg(H_2O)_6](SO_4)_2$ | $F(000) = 928$ |
| $M_r = 438.74$ | $D_x = 1.661$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 2014 reflections |
| $a = 14.968$ (3) Å | $\theta = 3.1$–$27.5°$ |
| $b = 9.1860$ (18) Å | $\mu = 0.41$ mm$^{-1}$ |
| $c = 14.334$ (3) Å | $T = 298$ K |
| $\beta = 117.12$ (3)° | Block, colorless |
| $V = 1754.2$ (8) Å$^3$ | $0.40 \times 0.30 \times 0.20$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Rigaku SCXmini CCD diffractometer | 8747 measured reflections |
| Radiation source: fine-focus sealed tube | 2014 independent reflections |
| Graphite monochromator | 1839 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 13.6612 pixels mm$^{-1}$ | $R_{int} = 0.022$ |
| $\omega$ scans | $\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$ |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) | $h = -19 \rightarrow 19$ |
| | $k = -11 \rightarrow 11$ |
| $T_{min} = 0.89$, $T_{max} = 0.95$ | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | $w = 1/[\sigma^2(F_o^2) + (0.0899P)^2 + 2.4679P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.169$ | |
| $S = 1.26$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2014 reflections | $\Delta\rho_{max} = 1.30$ e Å$^{-3}$ |
| 116 parameters | $\Delta\rho_{min} = -1.08$ e Å$^{-3}$ |
| 0 restraints | Extinction correction: *SHELXTL* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.045 (4) |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.61852 (4) | 0.24340 (6) | 0.11814 (4) | 0.0233 (3) |
| O1W | 0.17086 (15) | 0.3991 (2) | 0.04379 (17) | 0.0371 (5) |
| H1WA | 0.1091 | 0.3776 | 0.0197 | 0.056* |
| H1WB | 0.1876 | 0.4636 | 0.0913 | 0.056* |
| Mg1 | 0.2500 | 0.2500 | 0.0000 | 0.0216 (3) |
| O2W | 0.37984 (14) | 0.3255 (2) | 0.11889 (15) | 0.0352 (5) |
| H2WA | 0.4372 | 0.3244 | 0.1203 | 0.053* |
| H2WB | 0.3855 | 0.3321 | 0.1805 | 0.053* |
| O1 | 0.68789 (16) | 0.1296 (2) | 0.18242 (15) | 0.0383 (5) |
| O3W | 0.23727 (17) | 0.1023 (2) | 0.10262 (15) | 0.0397 (5) |
| H3WA | 0.2082 | 0.0203 | 0.0839 | 0.059* |

| | | | |
|---|---|---|---|
| H3WB | 0.2606 | 0.1142 | 0.1684 | 0.059* |
| O2 | 0.58702 (19) | 0.3346 (3) | 0.18142 (17) | 0.0490 (7) |
| N1 | −0.02189 (19) | 0.2779 (3) | 0.15657 (17) | 0.0352 (6) |
| H1 | −0.0387 | 0.2783 | 0.0870 | 0.042* |
| O3 | 0.52895 (16) | 0.1720 (3) | 0.03471 (16) | 0.0450 (6) |
| O4 | 0.66399 (19) | 0.3290 (2) | 0.06522 (19) | 0.0472 (6) |
| C1 | 0.0764 (3) | 0.2074 (5) | 0.2138 (3) | 0.0538 (9) |
| H1B | 0.1276 | 0.2641 | 0.2066 | 0.065* |
| H1C | 0.0748 | 0.1110 | 0.1855 | 0.065* |
| C2 | −0.1004 (3) | 0.1967 (5) | 0.1718 (3) | 0.0569 (10) |
| H2A | −0.1012 | 0.0955 | 0.1522 | 0.068* |
| H2B | −0.1660 | 0.2382 | 0.1283 | 0.068* |
| C3 | −0.0189 (4) | 0.4288 (4) | 0.1915 (3) | 0.0575 (10) |
| H3A | −0.0855 | 0.4713 | 0.1572 | 0.069* |
| H3B | 0.0254 | 0.4863 | 0.1734 | 0.069* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0256 (4) | 0.0261 (4) | 0.0189 (4) | −0.0006 (2) | 0.0108 (3) | −0.00084 (19) |
| O1W | 0.0286 (10) | 0.0394 (11) | 0.0437 (11) | −0.0001 (8) | 0.0166 (9) | −0.0157 (9) |
| Mg1 | 0.0226 (6) | 0.0232 (6) | 0.0179 (6) | 0.0001 (4) | 0.0085 (5) | −0.0008 (4) |
| O2W | 0.0254 (9) | 0.0532 (13) | 0.0245 (9) | −0.0056 (8) | 0.0091 (8) | −0.0064 (8) |
| O1 | 0.0425 (11) | 0.0411 (11) | 0.0247 (9) | 0.0132 (9) | 0.0095 (8) | 0.0013 (8) |
| O3W | 0.0609 (14) | 0.0335 (11) | 0.0253 (10) | −0.0144 (9) | 0.0203 (10) | −0.0001 (8) |
| O2 | 0.0632 (15) | 0.0555 (15) | 0.0317 (11) | 0.0207 (12) | 0.0247 (11) | −0.0024 (10) |
| N1 | 0.0370 (13) | 0.0521 (15) | 0.0166 (10) | 0.0083 (11) | 0.0122 (10) | 0.0022 (9) |
| O3 | 0.0314 (11) | 0.0643 (16) | 0.0304 (11) | −0.0149 (10) | 0.0064 (9) | −0.0022 (10) |
| O4 | 0.0637 (15) | 0.0410 (13) | 0.0503 (13) | −0.0170 (11) | 0.0378 (13) | −0.0022 (10) |
| C1 | 0.052 (2) | 0.073 (2) | 0.0464 (19) | 0.0296 (18) | 0.0312 (17) | 0.0097 (18) |
| C2 | 0.0463 (19) | 0.078 (3) | 0.0433 (19) | −0.0272 (19) | 0.0174 (15) | −0.0236 (18) |
| C3 | 0.080 (3) | 0.0389 (18) | 0.064 (2) | 0.0159 (17) | 0.042 (2) | 0.0226 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O4 | 1.458 (2) | O3W—H3WB | 0.8502 |
| S1—O2 | 1.462 (2) | N1—C3 | 1.467 (5) |
| S1—O1 | 1.466 (2) | N1—C1 | 1.469 (4) |
| S1—O3 | 1.482 (2) | N1—C2 | 1.490 (5) |
| O1W—Mg1 | 2.0856 (19) | N1—H1 | 0.9100 |
| O1W—H1WA | 0.8502 | C1—C2ii | 1.513 (5) |
| O1W—H1WB | 0.8500 | C1—H1B | 0.9700 |
| Mg1—O2W | 2.035 (2) | C1—H1C | 0.9700 |
| Mg1—O2Wi | 2.035 (2) | C2—C1ii | 1.513 (5) |
| Mg1—O3Wi | 2.0728 (19) | C2—H2A | 0.9700 |
| Mg1—O3W | 2.0728 (19) | C2—H2B | 0.9700 |
| Mg1—O1Wi | 2.0856 (19) | C3—C3ii | 1.506 (8) |
| O2W—H2WA | 0.8499 | C3—H3A | 0.9700 |

| | | | |
|---|---|---|---|
| O2W—H2WB | 0.8502 | C3—H3B | 0.9700 |
| O3W—H3WA | 0.8499 | | |
| | | | |
| O4—S1—O2 | 111.89 (16) | Mg1—O3W—H3WA | 123.8 |
| O4—S1—O1 | 110.28 (14) | Mg1—O3W—H3WB | 125.4 |
| O2—S1—O1 | 110.80 (12) | H3WA—O3W—H3WB | 110.9 |
| O4—S1—O3 | 106.49 (14) | C3—N1—C1 | 111.0 (3) |
| O2—S1—O3 | 109.00 (14) | C3—N1—C2 | 109.1 (3) |
| O1—S1—O3 | 108.21 (14) | C1—N1—C2 | 110.7 (3) |
| Mg1—O1W—H1WA | 112.8 | C3—N1—H1 | 108.7 |
| Mg1—O1W—H1WB | 134.3 | C1—N1—H1 | 108.7 |
| H1WA—O1W—H1WB | 110.8 | C2—N1—H1 | 108.7 |
| O2W—Mg1—O2W$^i$ | 180.00 (17) | N1—C1—C2$^{ii}$ | 108.5 (3) |
| O2W—Mg1—O3W$^i$ | 90.55 (9) | N1—C1—H1B | 110.0 |
| O2W$^i$—Mg1—O3W$^i$ | 89.45 (9) | C2$^{ii}$—C1—H1B | 110.0 |
| O2W—Mg1—O3W | 89.45 (9) | N1—C1—H1C | 110.0 |
| O2W$^i$—Mg1—O3W | 90.55 (9) | C2$^{ii}$—C1—H1C | 110.0 |
| O3W$^i$—Mg1—O3W | 180.00 (13) | H1B—C1—H1C | 108.4 |
| O2W—Mg1—O1W$^i$ | 91.10 (8) | N1—C2—C1$^{ii}$ | 108.2 (3) |
| O2W$^i$—Mg1—O1W$^i$ | 88.90 (8) | N1—C2—H2A | 110.1 |
| O3W$^i$—Mg1—O1W$^i$ | 88.14 (9) | C1$^{ii}$—C2—H2A | 110.1 |
| O3W—Mg1—O1W$^i$ | 91.86 (9) | N1—C2—H2B | 110.1 |
| O2W—Mg1—O1W | 88.90 (8) | C1$^{ii}$—C2—H2B | 110.1 |
| O2W$^i$—Mg1—O1W | 91.10 (8) | H2A—C2—H2B | 108.4 |
| O3W$^i$—Mg1—O1W | 91.86 (9) | N1—C3—C3$^{ii}$ | 108.51 (18) |
| O3W—Mg1—O1W | 88.14 (9) | N1—C3—H3A | 110.0 |
| O1W$^i$—Mg1—O1W | 180.00 (10) | C3$^{ii}$—C3—H3A | 110.0 |
| Mg1—O2W—H2WA | 125.8 | N1—C3—H3B | 110.0 |
| Mg1—O2W—H2WB | 119.9 | C3$^{ii}$—C3—H3B | 110.0 |
| H2WA—O2W—H2WB | 110.8 | H3A—C3—H3B | 108.4 |
| | | | |
| C3—N1—C1—C2$^{ii}$ | 64.8 (4) | C1—N1—C2—C1$^{ii}$ | 65.4 (4) |
| C2—N1—C1—C2$^{ii}$ | −56.5 (4) | C1—N1—C3—C3$^{ii}$ | −55.0 (5) |
| C3—N1—C2—C1$^{ii}$ | −57.0 (5) | C2—N1—C3—C3$^{ii}$ | 67.3 (5) |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O3$^i$ | 0.91 | 1.87 | 2.734 (3) | 157 |
| O1*W*—H1*WA*···O3$^i$ | 0.85 | 1.90 | 2.751 (3) | 179 |
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| O2*W*—H2*WB*···O2$^{iv}$ | 0.85 | 1.83 | 2.674 (3) | 173 |
| O3*W*—H3*WA*···O4$^v$ | 0.85 | 1.85 | 2.694 (3) | 170 |
| O3*W*—H3*WB*···O1$^{iv}$ | 0.85 | 1.92 | 2.769 (3) | 177 |

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*; (iii) *x*−1/2, *y*+1/2, *z*; (iv) −*x*+1, *y*, −*z*+1/2; (v) *x*−1/2, *y*−1/2, *z*.