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# Propane-1,3-diaminium bis(pyridine-4-carboxylate) monohydrate

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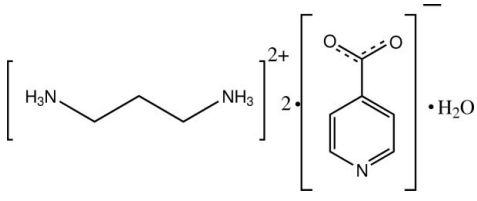
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.046; $wR$ factor = 0.122; data-to-parameter ratio = 18.4.

The asymmetric unit of the title compound, $C_3H_{12}N_2^{2+}\cdot 2C_6H_4NO_2^-\cdot H_2O$, consists of half of a doubly protonated propane-1,3-diammonium dication, a pyridine-4-carboxylate anion and half of a solvent water molecule; the dication and the solvent water are located on a twofold rotation axis which passes through the central C atom of the dication and the water O atom. The carboxylate group of the anion appears to be delocalized on the basis of the C—O bond lengths. In the crystal, the components are linked by intermolecular N—H···O, N—H···N and O—H···O hydrogen bonds.

## Related literature

For related compounds with a propane-1,3- diammonium dication which exhibit an all-*trans* zigzag conformation, see: Turner & Batten (2010); Aghabozorg *et al.*, (2011). For the preparation of the flexible ligand, see: Brito *et al.* (2010, 2011).




## Experimental

### Crystal data

$C_3H_{12}N_2^{2+}\cdot 2C_6H_4NO_2^-\cdot H_2O$
$M_r$ = 338.37
Monoclinic, $C2/c$
$a$ = 15.360 (3) Å
$b$ = 12.508 (3) Å
$c$ = 10.593 (2) Å
$\beta$ = 122.67 (3)°
$V$ = 1713.2 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 295 K
0.27 × 0.25 × 0.21 mm

### Data collection

Nonius KappaCCD area-detector diffractometer
11720 measured reflections
2119 independent reflections
1871 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.050

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.122
$S$ = 1.06
2119 reflections
115 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$A$···O1$^{i}$ | 0.89 | 1.91 | 2.7901 (16) | 170 |
| N2—H2$B$···O2$^{ii}$ | 0.89 | 1.91 | 2.779 (2) | 165 |
| N2—H2$C$···N1$^{iii}$ | 0.89 | 2.00 | 2.877 (2) | 166 |
| O3—H3···O1$^{iv}$ | 0.85 (2) | 2.00 (3) | 2.8426 (17) | 169 (2) |

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

Data collection: *COLLECT* (Nonius, 2000; cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008 ); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); 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: OM2459).

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# supporting information

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## Propane-1,3-diaminium bis(pyridine-4-carboxylate) monohydrate

**Iván Brito, Javier Vallejos, Alejandro Cárdenas and Matías López-Rodríguez**

### S1. Comment

This paper forms part of our continuing study of the synthesis and structural characterization of a flexible ligand for preparation of coordination polymers (Brito *et al.*, 2010; 2011 and references therein). The title compound was isolated during attempts to synthesize a flexible ligand by a condensation reaction between 4-pyridinecarboxylic acid and 1,3-diaminopropane. A notable feature of the structure is the extensive network of the hydrogen bonds between the ammonium H and pyridine-carboxylate N, O atoms. The hydrogen-bonding network involves all of the ammonium H and pyridine-carboxylate O,*N* atoms, forming a three-dimensional network Fig.2, Table 1. The water H are linked to two carboxylate O atoms at (-1/2 + *x*, 1/2 + *y*, *z*) and at (3/2 - *x*,1/2 + *y*, 3/2 - *z*) respectively, forming a two-dimensional network. Propane-1,3-diammonium dication has a fully extended all-*trans* zigzag conformation (N/C/C/C torsion angle 167.57 (13)°). The bond distances and angles for dication and anion are in normal range (Aghabozorg *et al.*, 2011; Turner & Batten 2010, as representative examples).

### S2. Experimental

To a solution of 4-pyridinecarboxylic acid (12.3 g, 0.1 mol) in pyridine (40 ml) was added 1,3-diaminopropane (3.71 g, 0,05 mol) in pyridine (20 ml). The solution was stirred gently for 15 min, forming a white precipitate. The resultant solution was then heated with stirring on the steam bath for 4 h. On cooling of the mixture, a white solid crystalline was obtained. Yield 15.8 g (92.9%). Analysis calculated for $C_{15}H_{22}N_4O_5$ (338.37 Dalton): C: 53.22, H: 6.52, N: 16.53; found: C: 52.97, H: 6.50, N: 16.90. IR (KBr, $cm^{-1}$): ($NH_3^+$) 1664 m, (C=C) 1600 m, ($NH_3^+$) 1500 m, ($CH_2$) 1378 w, ($NH_3^+$) 1155 m

### S3. Refinement

H3 atom was located directly from a Fourier map and refined freely. The positions of the remaining H atoms were located from difference maps and then treated as riding atoms, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.89 Å and with $U_{iso}$(H) values of 1.2$U_{eq}$(C, N).

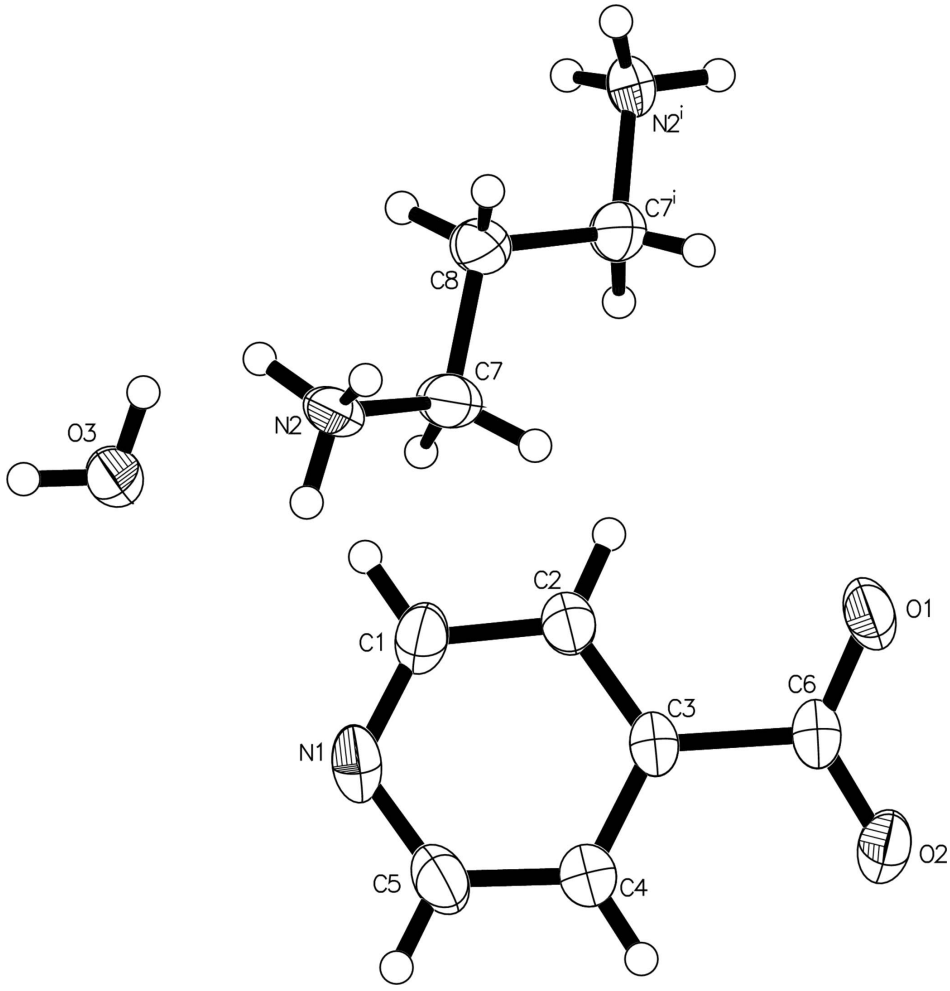


**Figure 1**

A view of the molecular structure of title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code i: 1 - *x*, *y*, 1/2 - *z*].

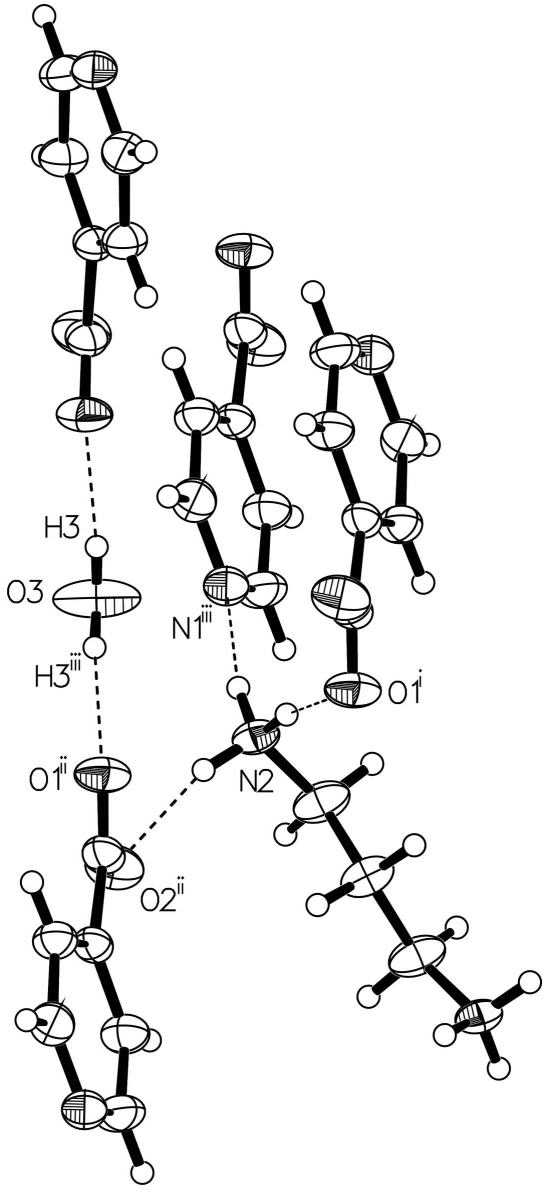


**Figure 2**

A view of title compound showing the hydrogen bonds and are indicated by dashed lines. [Symmetry codes: (i) *x* - 1/2, -*y* + 3/2, *z* - 1/2; (ii) -*x* + 3/2, *y* + 1/2, -*z* + 3/2; (iii) -*x* + 1, *y*, -*z* + 3/2; (iv) *x* - 1/2, *y* + 1/2, *z*]

**Propane-1,3-diaminium bis(pyridine-4-carboxylate) monohydrate**

*Crystal data*

$C_3H_{12}N_2^{2+}\cdot 2C_6H_4NO_2^-\cdot H_2O$
$M_r$ = 338.37
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 15.360 (3) Å
*b* = 12.508 (3) Å
*c* = 10.593 (2) Å
$\beta$ = 122.67 (3)°
*V* = 1713.2 (8) Å$^3$
*Z* = 4
*F*(000) = 720
$D_x$ = 1.312 Mg m$^{-3}$
Mo *K*$\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9511 reflections
$\theta$ = 3.9–28.5°
$\mu$ = 0.10 mm$^{-1}$

$T$ = 295 K
Block, colourless

0.27 × 0.25 × 0.21 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans with $\kappa$ offsets
11720 measured reflections
2119 independent reflections

1871 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.050
$\theta_{max}$ = 28.5°, $\theta_{min}$ = 4.0°
$h$ = −20→20
$k$ = −16→16
$l$ = −14→11

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.122
$S$ = 1.06
2119 reflections
115 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 1.0503P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| O1 | 0.87262 (8) | 0.51431 (8) | 0.82722 (12) | 0.0447 (3) | |
| O2 | 0.81345 (8) | 0.36420 (8) | 0.86906 (13) | 0.0480 (3) | |
| O3 | 0.5000 | 0.90541 (13) | 0.7500 | 0.0712 (6) | |
| H3 | 0.4617 (17) | 0.9452 (17) | 0.766 (2) | 0.072 (6)* | |
| N1 | 0.60893 (9) | 0.65138 (10) | 0.92600 (13) | 0.0405 (3) | |
| N2 | 0.48117 (8) | 0.79864 (8) | 0.46730 (12) | 0.0340 (3) | |
| H2A | 0.4411 | 0.8559 | 0.4258 | 0.041* | |
| H2B | 0.5458 | 0.8194 | 0.5334 | 0.041* | |
| H2C | 0.4579 | 0.7600 | 0.5136 | 0.041* | |
| C1 | 0.64814 (10) | 0.69083 (11) | 0.84955 (15) | 0.0389 (3) | |
| H1 | 0.6312 | 0.7605 | 0.8136 | 0.047* | |
| C2 | 0.71275 (10) | 0.63306 (11) | 0.82123 (14) | 0.0355 (3) | |
| H2 | 0.7383 | 0.6636 | 0.7675 | 0.043* | |
| C3 | 0.73892 (9) | 0.52889 (10) | 0.87425 (13) | 0.0301 (3) | |

| | | | | | |
|---|---|---|---|---|---|
| C4 | 0.69716 (10) | 0.48635 (11) | 0.95152 (16) | 0.0386 (3) | |
| H4 | 0.7115 | 0.4163 | 0.9866 | 0.046* | |
| C5 | 0.63370 (11) | 0.55061 (13) | 0.97516 (17) | 0.0437 (3) | |
| H5 | 0.6068 | 0.5220 | 1.0282 | 0.052* | |
| C6 | 0.81423 (9) | 0.46330 (10) | 0.85422 (14) | 0.0339 (3) | |
| C7 | 0.47907 (13) | 0.73319 (11) | 0.34918 (17) | 0.0431 (3) | |
| H7B | 0.4119 | 0.6993 | 0.2884 | 0.052* | |
| H7A | 0.5309 | 0.6773 | 0.3956 | 0.052* | |
| C8 | 0.5000 | 0.80121 (15) | 0.2500 | 0.0401 (4) | |
| H8A | 0.4408 | 0.8468 | 0.1876 | 0.048* | 0.50 |
| H8B | 0.5592 | 0.8468 | 0.3124 | 0.048* | 0.50 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0438 (5) | 0.0454 (6) | 0.0626 (7) | 0.0006 (4) | 0.0402 (5) | −0.0077 (5) |
| O2 | 0.0492 (6) | 0.0347 (5) | 0.0702 (7) | 0.0085 (4) | 0.0389 (6) | −0.0020 (5) |
| O3 | 0.0961 (14) | 0.0306 (8) | 0.146 (2) | 0.000 | 0.1046 (16) | 0.000 |
| N1 | 0.0363 (6) | 0.0498 (7) | 0.0401 (6) | 0.0113 (5) | 0.0237 (5) | −0.0029 (5) |
| N2 | 0.0406 (6) | 0.0330 (5) | 0.0414 (6) | −0.0052 (4) | 0.0306 (5) | 0.0008 (4) |
| C1 | 0.0392 (7) | 0.0383 (7) | 0.0402 (7) | 0.0127 (5) | 0.0220 (6) | 0.0027 (5) |
| C2 | 0.0361 (6) | 0.0375 (7) | 0.0393 (6) | 0.0060 (5) | 0.0246 (5) | 0.0030 (5) |
| C3 | 0.0264 (5) | 0.0332 (6) | 0.0320 (6) | 0.0027 (4) | 0.0165 (5) | −0.0045 (4) |
| C4 | 0.0402 (7) | 0.0371 (7) | 0.0469 (7) | 0.0049 (5) | 0.0289 (6) | 0.0036 (5) |
| C5 | 0.0438 (7) | 0.0528 (8) | 0.0483 (7) | 0.0067 (6) | 0.0340 (6) | 0.0031 (6) |
| C6 | 0.0298 (6) | 0.0366 (6) | 0.0371 (6) | 0.0048 (5) | 0.0194 (5) | −0.0049 (5) |
| C7 | 0.0649 (9) | 0.0301 (6) | 0.0561 (8) | −0.0059 (6) | 0.0469 (8) | −0.0024 (6) |
| C8 | 0.0597 (12) | 0.0308 (9) | 0.0484 (10) | 0.000 | 0.0413 (10) | 0.000 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C6 | 1.2531 (16) | C2—H2 | 0.9300 |
| O2—C6 | 1.2503 (17) | C3—C4 | 1.3896 (18) |
| O3—H3 | 0.85 (2) | C3—C6 | 1.5237 (15) |
| N1—C1 | 1.3373 (18) | C4—C5 | 1.3865 (18) |
| N1—C5 | 1.338 (2) | C4—H4 | 0.9300 |
| N2—C7 | 1.4809 (17) | C5—H5 | 0.9300 |
| N2—H2A | 0.8900 | C7—C8 | 1.5151 (16) |
| N2—H2B | 0.8900 | C7—H7B | 0.9700 |
| N2—H2C | 0.8900 | C7—H7A | 0.9700 |
| C1—C2 | 1.3851 (17) | C8—C7$^{i}$ | 1.5151 (16) |
| C1—H1 | 0.9300 | C8—H8A | 0.9700 |
| C2—C3 | 1.3897 (18) | C8—H8B | 0.9700 |
| | | | |
| C1—N1—C5 | 117.18 (11) | N1—C5—C4 | 123.75 (13) |
| C7—N2—H2A | 109.5 | N1—C5—H5 | 118.1 |
| C7—N2—H2B | 109.5 | C4—C5—H5 | 118.1 |
| H2A—N2—H2B | 109.5 | O2—C6—O1 | 126.17 (11) |

| | | | |
|---|---|---|---|
| C7—N2—H2C | 109.5 | O2—C6—C3 | 117.18 (11) |
| H2A—N2—H2C | 109.5 | O1—C6—C3 | 116.64 (12) |
| H2B—N2—H2C | 109.5 | N2—C7—C8 | 111.07 (11) |
| N1—C1—C2 | 123.24 (13) | N2—C7—H7B | 109.4 |
| N1—C1—H1 | 118.4 | C8—C7—H7B | 109.4 |
| C2—C1—H1 | 118.4 | N2—C7—H7A | 109.4 |
| C1—C2—C3 | 119.10 (12) | C8—C7—H7A | 109.4 |
| C1—C2—H2 | 120.5 | H7B—C7—H7A | 108.0 |
| C3—C2—H2 | 120.5 | C7$^{i}$—C8—C7 | 111.68 (15) |
| C4—C3—C2 | 118.18 (11) | C7$^{i}$—C8—H8A | 109.3 |
| C4—C3—C6 | 120.16 (12) | C7—C8—H8A | 109.3 |
| C2—C3—C6 | 121.62 (11) | C7$^{i}$—C8—H8B | 109.3 |
| C5—C4—C3 | 118.52 (13) | C7—C8—H8B | 109.3 |
| C5—C4—H4 | 120.7 | H8A—C8—H8B | 107.9 |
| C3—C4—H4 | 120.7 | | |

| | | | |
|---|---|---|---|
| C5—N1—C1—C2 | −0.7 (2) | C3—C4—C5—N1 | 0.9 (2) |
| N1—C1—C2—C3 | −0.1 (2) | C4—C3—C6—O2 | 20.19 (18) |
| C1—C2—C3—C4 | 1.19 (19) | C2—C3—C6—O2 | −162.03 (12) |
| C1—C2—C3—C6 | −176.62 (12) | C4—C3—C6—O1 | −158.46 (13) |
| C2—C3—C4—C5 | −1.6 (2) | C2—C3—C6—O1 | 19.31 (17) |
| C6—C3—C4—C5 | 176.26 (12) | N2—C7—C8—C7$^{i}$ | 167.76 (14) |
| C1—N1—C5—C4 | 0.2 (2) | | |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*A*···O1$^{ii}$ | 0.89 | 1.91 | 2.7901 (16) | 170 |
| N2—H2*B*···O2$^{iii}$ | 0.89 | 1.91 | 2.779 (2) | 165 |
| N2—H2*C*···N1$^{iv}$ | 0.89 | 2.00 | 2.877 (2) | 166 |
| O3—H3···O1$^{v}$ | 0.85 (2) | 2.00 (3) | 2.8426 (17) | 169 (2) |

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