

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 2,4-Diamino-6-methyl-1,3,5-triazin-1-ium hydrogen oxalate

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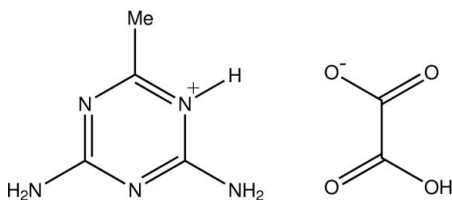
Received 9 March 2012; accepted 16 April 2012

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.041;  $wR$  factor = 0.113; data-to-parameter ratio = 13.5.

The title compound,  $\text{C}_4\text{H}_8\text{N}_5^+\cdot\text{C}_2\text{HO}_4^-$ , was obtained from the reaction of oxalic acid and 2,4-diamino-6-methyl-1,3,5-triazine. The protonated triazine ring is essentially planar with a maximum deviation of 0.035 (1) Å, but the hydrogen oxalate anion is less planar, with a maximum deviation of 0.131 (1) Å for both carbonyl O atoms. In the crystal, the ions are linked by intermolecular  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{N}$ ,  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, forming a three-dimensional network. Weak  $\pi-\pi$  [centroid-centroid distance = 3.763 Å] and  $\text{C}-\text{O}\cdots\pi$  interactions [ $\text{O}\cdots\text{centroid} = 3.5300$  (16) Å,  $\text{C}-\text{O}\cdots\text{centroid} = 132.19$  (10) $^\circ$ ] are also present.

### Related literature

For bond-length data see: Allen *et al.* (1987) and for a description of the Cambridge Structural Database, see: Allen (2002). For background to triazine derivatives, see: Sebenik *et al.* (1989). For related structures, see: Kaczmarek *et al.* (2008); Xiao (2008); Fan *et al.* (2009); Qian & Huang (2010).



### Experimental

#### Crystal data

$\text{C}_4\text{H}_8\text{N}_5^+\cdot\text{C}_2\text{HO}_4^-$   
 $M_r = 215.18$   
 Triclinic,  $P\bar{1}$   
 $a = 5.6208$  (12) Å  
 $b = 7.9828$  (17) Å  
 $c = 10.857$  (2) Å  
 $\alpha = 76.846$  (4) $^\circ$   
 $\beta = 75.882$  (4) $^\circ$

$\gamma = 75.954$  (4) $^\circ$   
 $V = 450.92$  (17) Å $^3$   
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.13$  mm $^{-1}$   
 $T = 298$  K  
 $0.50 \times 0.22 \times 0.19$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.935$ ,  $T_{\max} = 0.974$

5551 measured reflections  
 1959 independent reflections  
 1708 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.113$   
 $S = 1.03$   
 1959 reflections  
 145 parameters  
 1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.25$  e Å $^{-3}$   
 $\Delta\rho_{\text{min}} = -0.27$  e Å $^{-3}$

Table 1

 Hydrogen-bond geometry (Å,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O1}^{\text{i}}$	0.95 (2)	1.77 (2)	2.7134 (17)	174 (2)
$\text{N3}-\text{H3}\cdots\text{O4}^{\text{i}}$	0.95 (2)	2.50 (2)	2.9841 (17)	111.7 (16)
$\text{O4}-\text{H4}\cdots\text{O2}$	0.83 (2)	1.66 (2)	2.4921 (16)	175 (2)
$\text{N4}-\text{H4D}\cdots\text{O3}^{\text{ii}}$	0.86	2.17	2.9902 (19)	160
$\text{N4}-\text{H4E}\cdots\text{N1}^{\text{iii}}$	0.86	2.18	3.0399 (19)	174
$\text{N5}-\text{H5A}\cdots\text{N2}^{\text{iv}}$	0.86	2.14	3.0027 (19)	179
$\text{N5}-\text{H5B}\cdots\text{O2}^{\text{v}}$	0.86	2.28	2.8558 (17)	124
$\text{N5}-\text{H5B}\cdots\text{O3}^{\text{v}}$	0.86	2.59	3.2337 (19)	133
$\text{C4}-\text{H4C}\cdots\text{O1}^{\text{vi}}$	0.96	2.49	3.339 (2)	148

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 2009).

The authors would like to thank the Malaysian Government and Universiti Kebangsaan Malaysia for the research grants UKM-GUP-NBT-68-27-110.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2157).

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## supplementary materials

*Acta Cryst.* (2012). E68, o1475 [doi:10.1107/S1600536812016637]

**2,4-Diamino-6-methyl-1,3,5-triazin-1-ium hydrogen oxalate**

Leila Narimani and Bohari M. Yamin

**Comment**

It is known that many triazine derivatives possess biological properties beside its usefulness as intermediates in the pharmaceutical industry (Sebenik *et al.*, 1989). 2,4-diamino-6-methyl-1,3,5-triazine has been reported to co-crystallize with methanol (Kaczmarek *et al.*, 2008) and ethanol (Xiao, 2008). On the other hand, the triazine nitrogen atom at position 1 can be easily protonated as in compound  $(C_4H_8N_3)Cl$  (Qian & Huang, 2010) and  $(C_4H_8N_3)NO_3$  (Fan *et al.*, 2009) which were obtained from the normal acid-base reaction. The title compound is a similar salt but having a hydrogen oxalate as counter anion (Fig.1). The non hydrogen triazine ring, C1/N1/C2/N2/C3/N3, is planar with a maximum deviation of 0.035 (1) Å from the least square plane for N3 atom. The hydrogen oxalate anion O1/C1/O2/C2/O3/O4, is less planar with a maximum deviation of 0.131 (1) Å for O1 and O4 atoms. The bond lengths and angles are in normal ranges (Allen *et al.*, 1987; Allen, 2002). In the crystal structure the molecules are linked by N—H $\cdots$ O, N—H $\cdots$ N, O—H $\cdots$ O and C—H $\cdots$ O intermolecular hydrogen bonds (symmetry codes as in Table 2) to form a three-dimensional network (Fig. 2). In addition, there are weak  $\pi$ - $\pi$  interactions between the triazine ring centroids Cg1 (symmetry code: 1-x, -y, 1-z) with a distance of 3.763 Å and a C6—O3 $\cdots$  $\pi$  involving the triazine (C1/N1/C2/N2/C3/N3) centroid (symmetry code: 1-x, 1-y, 1-z) with a O3 $\cdots$ Cg1 distance of 3.5300 (16) Å and a C6—O3—Cg1 bond angle of 132.19 (10)°.

**Experimental**

10 ml aqueous solution of ammonium thiocyanate (0.152 g, 2 mmol) was added into a beaker containing oxalate acid (0.126 g, 1 mmol) and 2,4-diamino-6-methyl-1,3,5-triazine (2 mmol) in 40 ml distilled water. After one week of evaporation at room temperature colourless crystals were obtained. Yield 92%; Melting point: 457.1–458.3 K.

**Refinement**

After their location in the difference map, the H-atoms attached to the C and the amino N atoms were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C—H = 0.93 Å and N—H = 0.86 Å, and with  $U_{iso}(H) = 1.5U_{eq}(C)$  and  $1.2U_{eq}(N)$ . However, the protonated amino and hydroxyl hydrogen atoms were located from the Fourier map and refined isotropically.

**Computing details**

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

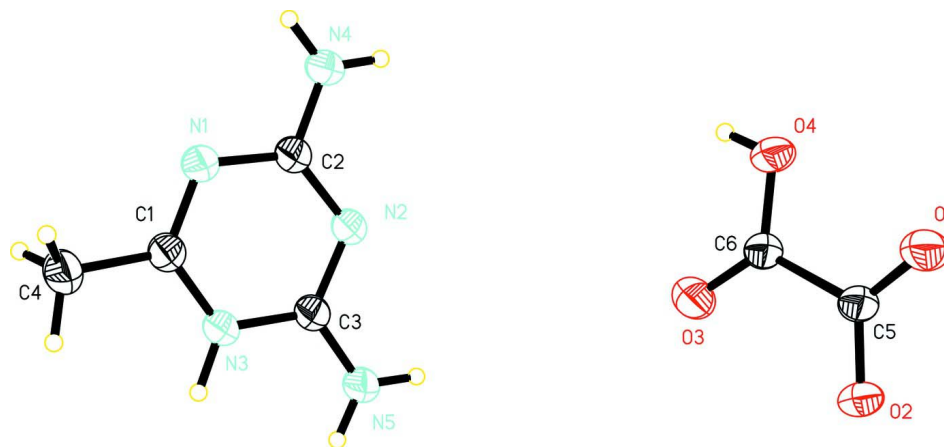


Figure 1

Molecular structure of the title compound with 50% probability displacement ellipsoids.

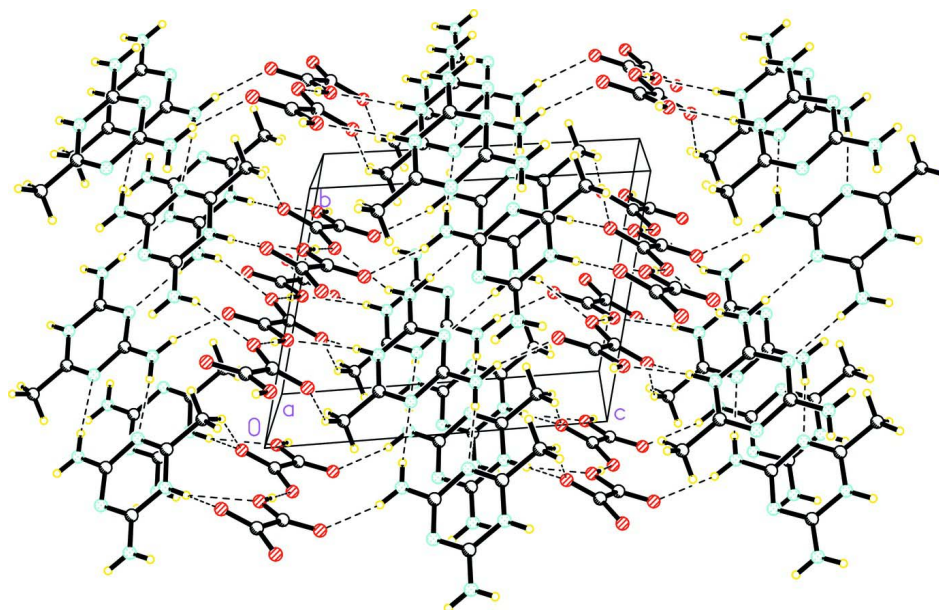


Figure 2

Packing diagram of the title compound viewed down *a* axis. The dashed lines denote hydrogen bonds.

### 2,4-Diamino-6-methyl-1,3,5-triazin-1-ium hydrogen oxalate

#### Crystal data

$C_4H_8N_5^+ \cdot C_2HO_4^-$   
 $M_r = 215.18$   
 Triclinic,  $P\bar{1}$   
 Hall symbol: -P 1  
 $a = 5.6208$  (12) Å  
 $b = 7.9828$  (17) Å  
 $c = 10.857$  (2) Å  
 $\alpha = 76.846$  (4)°  
 $\beta = 75.882$  (4)°  
 $\gamma = 75.954$  (4)°  
 $V = 450.92$  (17) Å<sup>3</sup>

$Z = 2$   
 $F(000) = 224$   
 $D_x = 1.585$  Mg m<sup>-3</sup>  
 Melting point = 492.2–492.5 K  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1963 reflections  
 $\theta = 1.9$ – $27.0$ °  
 $\mu = 0.13$  mm<sup>-1</sup>  
 $T = 298$  K  
 Block, colourless  
 $0.50 \times 0.22 \times 0.19$  mm

*Data collection*

Bruker SMART APEX CCD area-detector diffractometer	5551 measured reflections
Radiation source: fine-focus sealed tube	1959 independent reflections
Graphite monochromator	1708 reflections with $I > 2\sigma(I)$
Detector resolution: 83.66 pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.023$
$\omega$ scan	$\theta_{\text{max}} = 27.0^\circ$ , $\theta_{\text{min}} = 1.9^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.935$ , $T_{\text{max}} = 0.974$	$k = -10 \rightarrow 10$
	$l = -13 \rightarrow 13$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.113$	$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.0976P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1959 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
145 parameters	$\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.01323 (19)	0.22067 (16)	1.09284 (10)	0.0435 (3)
O2	1.20977 (17)	0.36561 (14)	0.91142 (9)	0.0383 (3)
O3	0.8189 (2)	0.38620 (18)	0.80042 (10)	0.0490 (3)
O4	0.60164 (18)	0.30135 (15)	0.99698 (10)	0.0401 (3)
H4	0.476 (3)	0.322 (3)	0.964 (2)	0.076 (7)*
N1	0.2651 (2)	0.08398 (15)	0.40173 (11)	0.0342 (3)
N2	0.3693 (2)	0.31924 (15)	0.46944 (11)	0.0326 (3)
N3	0.5937 (2)	0.21615 (15)	0.28003 (11)	0.0324 (3)
H3	0.733 (4)	0.221 (2)	0.2103 (19)	0.049 (5)*
N4	0.0411 (2)	0.18887 (17)	0.58245 (12)	0.0421 (3)
H4D	0.0102	0.2572	0.6377	0.051*
H4E	-0.0506	0.1130	0.5922	0.051*
N5	0.7025 (2)	0.43757 (17)	0.34456 (12)	0.0393 (3)
H5A	0.6827	0.5064	0.3983	0.047*
H5B	0.8206	0.4415	0.2771	0.047*
C1	0.4493 (3)	0.09606 (17)	0.30219 (13)	0.0307 (3)

C2	0.2280 (3)	0.20042 (18)	0.48339 (13)	0.0316 (3)
C3	0.5530 (3)	0.32675 (18)	0.36537 (12)	0.0302 (3)
C4	0.5070 (3)	-0.0268 (2)	0.21033 (15)	0.0400 (4)
H4A	0.5078	-0.1442	0.2574	0.060*
H4B	0.6685	-0.0204	0.1560	0.060*
H4C	0.3822	0.0048	0.1580	0.060*
C5	1.0268 (2)	0.30348 (18)	0.98158 (13)	0.0296 (3)
C6	0.8009 (2)	0.33563 (18)	0.91548 (13)	0.0301 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0288 (5)	0.0646 (7)	0.0332 (6)	-0.0124 (5)	-0.0051 (4)	0.0009 (5)
O2	0.0237 (5)	0.0565 (7)	0.0344 (6)	-0.0147 (4)	-0.0014 (4)	-0.0052 (5)
O3	0.0351 (6)	0.0828 (9)	0.0297 (6)	-0.0157 (6)	-0.0046 (4)	-0.0093 (5)
O4	0.0234 (5)	0.0622 (7)	0.0351 (6)	-0.0161 (5)	-0.0038 (4)	-0.0035 (5)
N1	0.0374 (7)	0.0359 (6)	0.0315 (6)	-0.0161 (5)	0.0015 (5)	-0.0103 (5)
N2	0.0381 (6)	0.0360 (6)	0.0262 (6)	-0.0158 (5)	0.0009 (5)	-0.0091 (5)
N3	0.0344 (6)	0.0375 (6)	0.0265 (6)	-0.0140 (5)	0.0022 (5)	-0.0097 (5)
N4	0.0467 (7)	0.0500 (8)	0.0340 (7)	-0.0264 (6)	0.0091 (5)	-0.0165 (6)
N5	0.0447 (7)	0.0487 (7)	0.0297 (6)	-0.0263 (6)	0.0048 (5)	-0.0124 (5)
C1	0.0338 (7)	0.0308 (6)	0.0282 (7)	-0.0090 (5)	-0.0039 (5)	-0.0061 (5)
C2	0.0353 (7)	0.0343 (7)	0.0263 (7)	-0.0126 (6)	-0.0019 (5)	-0.0064 (5)
C3	0.0338 (7)	0.0337 (7)	0.0241 (6)	-0.0117 (5)	-0.0031 (5)	-0.0045 (5)
C4	0.0471 (9)	0.0389 (8)	0.0360 (8)	-0.0132 (6)	0.0003 (6)	-0.0147 (6)
C5	0.0222 (6)	0.0375 (7)	0.0291 (7)	-0.0064 (5)	-0.0002 (5)	-0.0110 (5)
C6	0.0247 (6)	0.0381 (7)	0.0289 (7)	-0.0084 (5)	-0.0013 (5)	-0.0103 (5)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C5	1.2322 (17)	N4—C2	1.3112 (18)
O2—C5	1.2560 (16)	N4—H4D	0.8600
O3—C6	1.2093 (17)	N4—H4E	0.8600
O4—C6	1.2913 (16)	N5—C3	1.3104 (18)
O4—H4	0.831 (10)	N5—H5A	0.8600
N1—C1	1.3054 (18)	N5—H5B	0.8600
N1—C2	1.3727 (17)	C1—C4	1.4812 (19)
N2—C3	1.3329 (17)	C4—H4A	0.9600
N2—C2	1.3400 (17)	C4—H4B	0.9600
N3—C1	1.3465 (17)	C4—H4C	0.9600
N3—C3	1.3643 (18)	C5—C6	1.5476 (19)
N3—H3	0.950 (19)		
C6—O4—H4	113.8 (16)	N2—C2—N1	124.86 (12)
C1—N1—C2	116.03 (12)	N5—C3—N2	120.67 (12)
C3—N2—C2	116.42 (11)	N5—C3—N3	118.55 (12)
C1—N3—C3	119.67 (12)	N2—C3—N3	120.76 (12)
C1—N3—H3	122.3 (11)	C1—C4—H4A	109.5
C3—N3—H3	117.8 (11)	C1—C4—H4B	109.5
C2—N4—H4D	120.0	H4A—C4—H4B	109.5

C2—N4—H4E	120.0	C1—C4—H4C	109.5
H4D—N4—H4E	120.0	H4A—C4—H4C	109.5
C3—N5—H5A	120.0	H4B—C4—H4C	109.5
C3—N5—H5B	120.0	O1—C5—O2	127.05 (13)
H5A—N5—H5B	120.0	O1—C5—C6	118.95 (12)
N1—C1—N3	122.20 (12)	O2—C5—C6	113.99 (12)
N1—C1—C4	119.85 (12)	O3—C6—O4	126.24 (13)
N3—C1—C4	117.95 (12)	O3—C6—C5	121.73 (12)
N4—C2—N2	119.38 (12)	O4—C6—C5	112.03 (11)
N4—C2—N1	115.75 (12)		
C2—N1—C1—N3	-0.4 (2)	C2—N2—C3—N5	-179.22 (13)
C2—N1—C1—C4	178.65 (13)	C2—N2—C3—N3	-1.0 (2)
C3—N3—C1—N1	1.8 (2)	C1—N3—C3—N5	177.20 (13)
C3—N3—C1—C4	-177.27 (13)	C1—N3—C3—N2	-1.1 (2)
C3—N2—C2—N4	-178.67 (14)	O1—C5—C6—O3	-166.01 (14)
C3—N2—C2—N1	2.5 (2)	O2—C5—C6—O3	13.0 (2)
C1—N1—C2—N4	179.32 (13)	O1—C5—C6—O4	13.65 (18)
C1—N1—C2—N2	-1.8 (2)	O2—C5—C6—O4	-167.33 (12)

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>
N3—H3...O1 <sup>i</sup>	0.95 (2)	1.77 (2)	2.7134 (17)	174 (2)
N3—H3...O4 <sup>i</sup>	0.95 (2)	2.50 (2)	2.9841 (17)	111.7 (16)
O4—H4...O2	0.83 (2)	1.66 (2)	2.4921 (16)	175 (2)
N4—H4D...O3 <sup>ii</sup>	0.86	2.17	2.9902 (19)	160
N4—H4E...N1 <sup>iii</sup>	0.86	2.18	3.0399 (19)	174
N5—H5A...N2 <sup>iv</sup>	0.86	2.14	3.0027 (19)	179
N5—H5B...O2 <sup>v</sup>	0.86	2.28	2.8558 (17)	124
N5—H5B...O3 <sup>v</sup>	0.86	2.59	3.2337 (19)	133
C4—H4C...O1 <sup>vi</sup>	0.96	2.49	3.339 (2)	148

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