Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 2-[(carbamoylamino)imino]-propanoate hemihydrate

Charlane C. Corrêa,[a]* José Eugênio J. C. Graúdo,[a] Luiz Fernando C. de Oliveira,[a] Mauro V. de Almeida[b] and Renata Diniz[a]

[a]Núcleo de Espectroscopia e Estrutura Molecular (NEEM), Department of Chemistry - Federal University of Juiz de Fora - Minas Gerais, 36036-900, Brazil, and [b]Department of Chemistry - Federal University of Juiz de Fora - Minas Gerais, 36036-900, Brazil
Correspondence e-mail: charcorrea@gmail.com

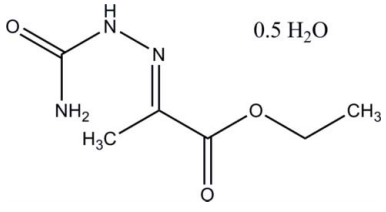
Received 7 June 2011; accepted 27 June 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.059; wR factor = 0.137; data-to-parameter ratio = 16.6.

The title compound, $C_6H_{11}N_3O_3\cdot0.5H_2O$, has two independent molecules and one molecule of water in the asymmetric unit. The crystal packing is stabilized by intermolecular N—H···N, O—H···O, N—H···O and C—H···O hydrogen bonds. These interactions form a two-dimensional array in the *ab* plane with a zigzag motif which has an angle close to 35° between the zigzag planes. The hydrogen bonding can be best described using the graph-set notation as $N_1 = C(10)R_2^2(10)R_2^2(8)$ and $N_2 = R_6^4(20)R_2^2(8)$.

Related literature

For the synthesis and applications of ethyl pyruvate semicarbazone, see: Kulka (1946); Dimmock *et al.* (1993); Cerecetto *et al.* (2000); Armor (1992). For hydrogen-bond motifs, see: Etter *et al.* (1990).



Experimental

Crystal data

$C_6H_{11}N_3O_3\cdot0.5H_2O$
M_r = 182.19
Monoclinic, $P2_1/n$
a = 11.173 (2) Å
b = 14.756 (3) Å
c = 11.565 (2) Å
β = 103.14 (3)°
V = 1856.8 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 293 K
0.21 × 0.10 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
18093 measured reflections
4228 independent reflections
1816 reflections with $I > 2\sigma(I)$
R_{int} = 0.109

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.137
S = 1.00
4228 reflections
255 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4*N*1···O1	0.85 (3)	2.19 (3)	3.030 (3)	166 (3)
N1—H1*N*1···O4	0.86 (3)	2.14 (3)	2.989 (3)	169 (3)
N2—H2*N*···O4^{i}	0.84 (2)	2.09 (2)	2.920 (3)	169 (2)
N4—H4*N*2···O7^{ii}	0.92 (3)	2.05 (3)	2.950 (3)	169 (3)
N1—H1*N*2···N3	0.88 (3)	2.31 (3)	2.656 (3)	103.5 (18)
N1—H1*N*2···O7	0.88 (3)	2.10 (3)	2.955 (3)	163 (3)
N5—H5*N*···O1^{iii}	0.84 (2)	2.11 (2)	2.935 (3)	167 (2)
O7—H7*A*···O2	0.92	1.92	2.809 (3)	163
O7—H7*B*···O5^{iv}	0.88	2.01	2.826 (3)	153
C6—H6*C*···O4^{i}	0.96	2.47	3.397 (3)	162

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

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009).

The authors thank CNPq, CAPES, and FAPEMIG (Brazilian agencies) for financial support and also R. G. Bastos (LDRX-IF/UFF) for the X-ray diffraction facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2011).

References

Armor, J. N. (1992). *Appl. Catal.* **B10**, 221–256.
Cerecetto, H., Di Maio, R., Gonzalez, M., Risso, M., Sagrera, G., Seoane, G., Denicola, A., Peluffo, G., Quijano, C., Stoppani, A. O. M., Paulino, M., Olea-Azar, C. & Basombrio, M. A. (2000). *Eur. J. Med. Chem.* **35**, 343–350.
Dimmock, J. R., Sidhu, K. K., Thayer, R. S., Mack, P., Dutty, M. J., Reid, R. S. & Quail, J. W. (1993). *J. Med. Chem.* **36**, 2243–2252.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Hooft, R. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Kulka, M. (1946). *Can. J. Res.* **24B**, 221—223.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2011). E**67**, o1882 [doi:10.1107/S160053681102530X]

Ethyl 2-[(carbamoylamino)imino]propanoate hemihydrate

Charlane C. Corrêa, José Eugênio J. C. Graúdo, Luiz Fernando C. de Oliveira, Mauro V. de Almeida and Renata Diniz

S1. Comment

Semicarbazones have been important in the consistent advances in design of novel anticonvulsant agents through the work of Dimmock *et al.* (Dimmock,1993); the aryl semicarbazone 4-bromobenzaldehyde semicarbazone has been a standard anticonvulsant drug selected by the National Institutes of Health, USA. They can also be used as drugs for Chagas's disease (Cerecetto, 2000) as well as hypnotic, pesticide and herbicide uses (Armor, 1992). The synthesis of ethyl pyruvate semicarbazone (**spe**) (Scheme I) was reported more than 60 years (Kulka, 1946); but to date the structure determination has not been reported. This structure will permit further study of the metal coordination properties of these interesting ligands.

Figure 1 shows the *ORTEP* representation of the asymmetric unit of **spe**. There are two crystallographically independent molecules and one water of crystallization in the asymmetric unit. The main differences between these molecules are the distances involved in the hydrogen bonds between [O4···H1N1···N1 = 2.989 (3) Å; O1···H4N1···N4 = 3.030 (3) Å; O7···H1N2···N1 = 2.955 (3) Å and $O7^{i}$···H4N2···N4 = 2.950 (3) Å] *(symmetry code: i: x - 1/2, -y + 1/2, z + 1/2)* and also by the torsion angles between the groups CH_3 and CH_2 [C10—O6—C9—O5 = 0.8 (4)° and C4—O3—C3—O2 =-1.3 (4)°; C10—O6—C9—C8 = -179.00 (2)° and C4—O3—C3—C2 = 179,60 (2)°; C12—C8—C9—O5 = -178.90 (3)° and C6—C2—C3—O2 = - 173.10 (3)°; C12—C8—C9—O6 = 1.0 (4)° and C6—C2—C3—O3 = 6.0 (3)°]. The water molecule of crystallization stabilizes the crystal lattice by the intermolecular hydrogen bonds N—H···N, O—H···O and O—H···N, with average distances between the electronegative atoms of: 2.656 (3), 2.818 (3), 2.963 (3) Å, respectively. The hydrogen bonding scheme is displayed in Figure 2 and using the graph-set notation the system can be best described as N_1=C(10)R_2^2(10)R_2^2(8) and N_2=R_6^4(20)R_2^2(8) (Etter, 1990).

There are two isomeric forms for compounds derived from ethyl pyruvate semicarbazone namely the *E* and *Z* isomers. The present structure is clearly the *E* form, Figures 1 and 2. The molecules of **spe** form a two-dimensional array in the *ab* plane with a zigzag motif which has an angle close to 35° between the zigzag planes.

S2. Experimental

For the preparation of ethyl pyruvate semicarbazone **spe**, 50 ml of an aqueous solution of semicarbazide chloride (1.019 g, 9.14 mmol) was added to a 50 ml of an ethanolic solution of ethylpyruvate (1.060 g, 9.14 mmol) and amonium acetate (0.744 g, 9.66 mmol), and the final mixture was heated at 80 °C for 6 h. Colorless crystals were formed. The compound decomposes at 175 °C. Elemental analysis gave the following results: Anal. Calcd. for $C_6H_{13}O_4N_3$: C,37,69; H,6,85; N,21,98%; Found: C,38,33; H,5,85; N,22,09%. Infrared spectra show absorption bands at 3506–3170 cm^{-1} (*ν*NH + *ν*OH); 1698 cm^{-1} (*ν*CO); 1599 cm^{-1} (*ν*NH + *ν*CN + *ν*CC); 1480 cm^{-1}(*ν*COasym); 1357 cm^{-1} (*ν*CN); 1144 cm^{-1} (*ν*COsym) and 1103 cm^{-1} (*ν*COC).

S3. Refinement

C-bound H atoms were included using the riding model approximation with C—H = 0.95 Å, with a common *U*_iso_(H). The H atoms of the water molecule were located from an electron density map, fixed in these positions and assigned the same isotropic displacement as the other H atoms.

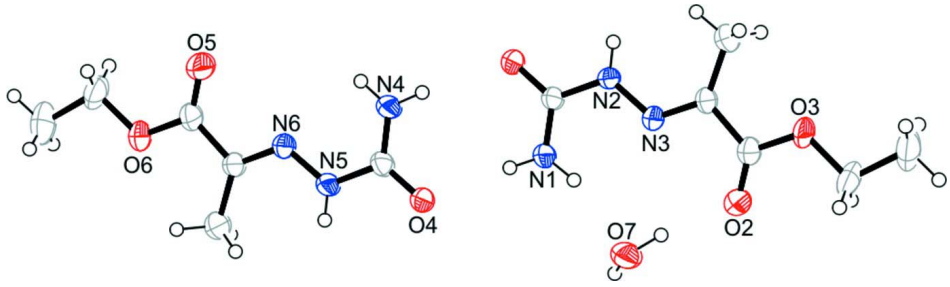


Figure 1

View *ORTEP* of crystal structure of compound **spe**.

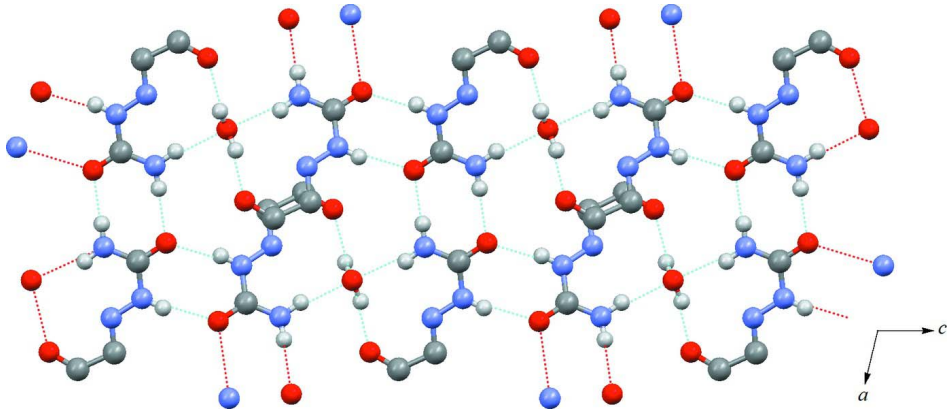


Figure 2

Hydrogen bonds between molecules of ethyl pyruvate semicarbazone and the water molecule, elucidating the ring formed by hydrogen bonds.

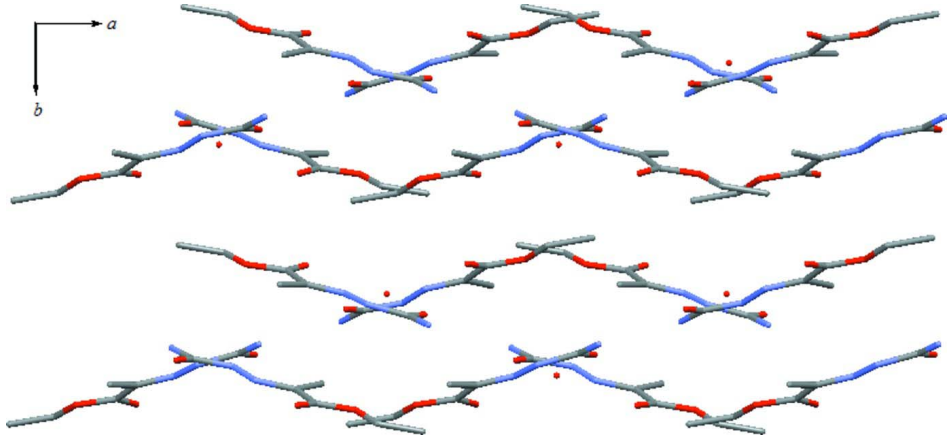


Figure 3

Crystal packing of compound **spe**, viewed along the *c* axis.

Ethyl 2-[(carbamoylamino)imino]propanoate hydrate

Crystal data

$C_6H_{11}N_3O_3 \cdot 0.5H_2O$
$M_r = 182.19$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 11.173$ (2) Å
$b = 14.756$ (3) Å
$c = 11.565$ (2) Å
$\beta = 103.14$ (3)°
$V = 1856.8$ (6) Å^3
$Z = 8$
$F(000) = 776$
$D_x = 1.303$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 33 reflections
$\theta = 4.5$–$18.2°$
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Prism, colourless
0.21 × 0.10 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD scans
18093 measured reflections
4228 independent reflections
1816 reflections with $I > 2\sigma(I)$
$R_{int} = 0.109$
$\theta_{max} = 27.5°$, $\theta_{min} = 5.2°$
$h = -13 \rightarrow 14$
$k = -18 \rightarrow 19$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.137$
$S = 1.00$
4228 reflections
255 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
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.5582P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0059 (11)
Absolute structure: no

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N6	0.63805 (17)	0.15088 (15)	0.54625 (17)	0.0361 (5)
O4	0.88839 (14)	0.22111 (13)	0.43482 (14)	0.0462 (5)

O1	1.12914 (15)	0.27042 (14)	0.71551 (14)	0.0482 (5)
N5	0.70387 (18)	0.17912 (16)	0.4671 (2)	0.0387 (6)
N2	1.31214 (18)	0.31483 (16)	0.6804 (2)	0.0394 (6)
N3	1.37693 (17)	0.34035 (15)	0.59917 (16)	0.0347 (5)
O6	0.34452 (15)	0.08529 (13)	0.56959 (15)	0.0493 (5)
O3	1.66804 (14)	0.40150 (13)	0.56711 (15)	0.0451 (5)
O7	1.25278 (16)	0.33845 (15)	0.32243 (15)	0.0577 (6)
H7A	1.3224	0.3672	0.3643	0.087*
H7B	1.1933	0.3754	0.2876	0.087*
C8	0.5218 (2)	0.13447 (18)	0.5091 (2)	0.0339 (6)
N1	1.1427 (2)	0.29295 (18)	0.52453 (19)	0.0458 (7)
C1	1.1895 (2)	0.29159 (18)	0.6407 (2)	0.0337 (6)
C2	1.4919 (2)	0.36056 (17)	0.6338 (2)	0.0333 (6)
C7	0.8274 (2)	0.19917 (18)	0.5083 (2)	0.0370 (7)
O5	0.51752 (17)	0.09562 (17)	0.71042 (17)	0.0733 (7)
O2	1.49015 (16)	0.39939 (15)	0.42999 (16)	0.0612 (6)
N4	0.8733 (2)	0.19408 (19)	0.6242 (2)	0.0503 (7)
C9	0.4642 (2)	0.10351 (19)	0.6078 (2)	0.0420 (7)
C3	1.5468 (2)	0.38847 (19)	0.5318 (2)	0.0397 (7)
C10	0.2801 (2)	0.0561 (2)	0.6597 (3)	0.0576 (9)
H10A	0.2850	0.1026	0.7199	0.069*
H10B	0.3167	0.0010	0.6978	0.069*
C12	0.4459 (2)	0.1434 (2)	0.3850 (2)	0.0542 (8)
H12A	0.4931	0.1239	0.3298	0.081*
H12B	0.4223	0.2056	0.3696	0.081*
H12C	0.3736	0.1065	0.3759	0.081*
C11	0.1485 (3)	0.0396 (2)	0.5977 (3)	0.0725 (10)
H11A	0.1141	0.0941	0.5584	0.109*
H11B	0.1026	0.0221	0.6549	0.109*
H11C	0.1446	−0.0079	0.5403	0.109*
C5	1.8633 (3)	0.4440 (2)	0.5311 (3)	0.0700 (10)
H5A	1.8705	0.4941	0.5852	0.105*
H5B	1.9075	0.4575	0.4709	0.105*
H5C	1.8971	0.3906	0.5735	0.105*
C4	1.7302 (2)	0.4283 (2)	0.4739 (3)	0.0533 (8)
H4A	1.6936	0.4833	0.4354	0.064*
H4B	1.7223	0.3809	0.4145	0.064*
C6	1.5688 (2)	0.3594 (2)	0.7578 (2)	0.0595 (9)
H6A	1.6120	0.4159	0.7742	0.089*
H6B	1.6270	0.3106	0.7661	0.089*
H6C	1.5169	0.3509	0.8126	0.089*
H2N	1.344 (2)	0.3065 (15)	0.753 (2)	0.026 (7)*
H4N1	0.949 (3)	0.2061 (19)	0.653 (2)	0.061 (9)*
H1N1	1.066 (3)	0.2794 (19)	0.501 (2)	0.055 (9)*
H5N	0.672 (2)	0.1881 (19)	0.395 (2)	0.056 (9)*
H4N2	0.826 (3)	0.1839 (18)	0.678 (2)	0.051 (8)*
H1N2	1.190 (3)	0.3057 (18)	0.475 (2)	0.048 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N6	0.0261 (11)	0.0499 (15)	0.0330 (12)	−0.0012 (10)	0.0084 (9)	0.0002 (10)
O4	0.0291 (9)	0.0795 (15)	0.0315 (10)	−0.0106 (10)	0.0100 (8)	−0.0059 (10)
O1	0.0293 (9)	0.0856 (16)	0.0318 (10)	−0.0126 (10)	0.0115 (8)	−0.0038 (10)
N5	0.0262 (11)	0.0616 (17)	0.0279 (12)	−0.0037 (11)	0.0054 (10)	−0.0026 (12)
N2	0.0243 (11)	0.0687 (18)	0.0248 (12)	−0.0053 (11)	0.0048 (9)	0.0055 (12)
N3	0.0262 (11)	0.0472 (15)	0.0316 (12)	−0.0042 (10)	0.0082 (9)	0.0021 (10)
O6	0.0295 (9)	0.0687 (14)	0.0507 (11)	−0.0117 (10)	0.0113 (8)	0.0018 (10)
O3	0.0249 (9)	0.0636 (14)	0.0499 (11)	−0.0033 (9)	0.0150 (8)	0.0059 (10)
O7	0.0378 (10)	0.0966 (16)	0.0365 (9)	0.0016 (11)	0.0036 (8)	−0.0013 (11)
C8	0.0269 (13)	0.0424 (17)	0.0326 (14)	0.0004 (12)	0.0071 (11)	0.0002 (12)
N1	0.0259 (12)	0.081 (2)	0.0305 (13)	−0.0111 (13)	0.0063 (11)	−0.0008 (12)
C1	0.0244 (13)	0.0485 (18)	0.0287 (14)	−0.0020 (12)	0.0071 (11)	−0.0032 (12)
C2	0.0227 (12)	0.0410 (17)	0.0366 (14)	0.0009 (12)	0.0073 (10)	0.0007 (12)
C7	0.0266 (13)	0.0505 (19)	0.0336 (15)	−0.0015 (13)	0.0062 (12)	−0.0056 (13)
O5	0.0409 (11)	0.132 (2)	0.0447 (12)	−0.0193 (13)	0.0040 (10)	0.0239 (13)
O2	0.0401 (11)	0.1044 (18)	0.0385 (11)	−0.0128 (12)	0.0076 (9)	0.0136 (11)
N4	0.0290 (13)	0.093 (2)	0.0281 (13)	−0.0114 (13)	0.0049 (11)	−0.0015 (13)
C9	0.0288 (14)	0.052 (2)	0.0444 (17)	−0.0046 (13)	0.0061 (12)	0.0043 (14)
C3	0.0295 (14)	0.0485 (19)	0.0423 (16)	−0.0007 (13)	0.0107 (12)	0.0012 (14)
C10	0.0437 (17)	0.071 (2)	0.065 (2)	−0.0103 (16)	0.0258 (15)	0.0107 (17)
C12	0.0320 (15)	0.084 (2)	0.0445 (17)	−0.0064 (15)	0.0040 (13)	0.0101 (16)
C11	0.0404 (17)	0.077 (3)	0.106 (3)	−0.0113 (17)	0.0272 (18)	0.005 (2)
C5	0.0455 (17)	0.081 (3)	0.093 (2)	−0.0205 (17)	0.0336 (17)	−0.013 (2)
C4	0.0407 (16)	0.061 (2)	0.066 (2)	−0.0024 (15)	0.0293 (15)	0.0131 (16)
C6	0.0288 (14)	0.104 (3)	0.0435 (17)	−0.0072 (16)	0.0042 (13)	0.0098 (17)

Geometric parameters (Å, º)

N6—C8	1.295 (3)	O7—H7B	0.8700
N6—N5	1.363 (3)	N1—H1N1	0.86 (3)
O4—C7	1.246 (3)	N1—H1N2	0.88 (3)
O1—C1	1.252 (3)	N2—H2N	0.84 (2)
N5—C7	1.386 (3)	N5—H5N	0.84 (2)
N2—N3	1.363 (3)	N4—H4N1	0.85 (3)
N2—C1	1.386 (3)	N4—H4N2	0.92 (3)
N3—C2	1.291 (3)	C5—H5C	0.9600
O6—C9	1.337 (3)	C5—H5A	0.9600
O6—C10	1.460 (3)	C5—H5B	0.9600
O3—C3	1.337 (3)	C4—H4A	0.9700
O3—C4	1.463 (3)	C4—H4B	0.9700
C8—C12	1.498 (3)	C6—H6C	0.9600
C8—C9	1.503 (3)	C6—H6A	0.9600
N1—C1	1.326 (3)	C6—H6B	0.9600
C2—C6	1.495 (3)	C11—H11A	0.9600
C2—C3	1.505 (3)	C11—H11B	0.9600

C7—N4	1.324 (3)	C11—H11C	0.9600
O5—C9	1.207 (3)	C10—H10A	0.9700
O2—C3	1.215 (3)	C10—H10B	0.9700
C10—C11	1.502 (4)	C12—H12A	0.9600
C5—C4	1.502 (4)	C12—H12B	0.9600
O7—H7A	0.9100	C12—H12C	0.9600
O1···N5^{i}	2.935 (3)	O5···O7^{iv}	2.826 (3)
O1···C12^{i}	3.388 (3)	O7···O5^{v}	2.826 (3)
O1···N4	3.030 (3)	O7···N6^{v}	3.164 (3)
O2···C3^{ii}	3.201 (4)	O7···O2	2.809 (3)
O2···O7	2.809 (3)	O7···N1	2.955 (3)
O2···N3	2.704 (3)	O7···N3	3.186 (3)
O4···N1	2.989 (3)	O7···N4^{v}	2.950 (3)
O4···C6^{iii}	3.397 (3)	N1···N3	2.656 (3)
O4···N2^{iii}	2.920 (3)	N4···N6	2.655 (3)
O5···N6	2.692 (3)		
C8—N6—N5	119.2 (2)	C7—N4—H4N1	120.3 (16)
N6—N5—C7	118.8 (2)	C7—N4—H4N2	123.1 (16)
N3—N2—C1	118.7 (2)	H5A—C5—H5B	109.00
C2—N3—N2	119.8 (2)	H5B—C5—H5C	109.00
C9—O6—C10	116.3 (2)	H5A—C5—H5C	110.00
C3—O3—C4	115.6 (2)	C4—C5—H5C	109.00
N6—C8—C12	127.4 (2)	C4—C5—H5B	109.00
N6—C8—C9	112.1 (2)	O3—C4—H4A	110.00
C12—C8—C9	120.5 (2)	O3—C4—H4B	110.00
O1—C1—N1	123.6 (2)	H4A—C4—H4B	109.00
O1—C1—N2	118.7 (2)	C5—C4—H4A	110.00
N1—C1—N2	117.7 (2)	C5—C4—H4B	110.00
N3—C2—C6	127.6 (2)	C2—C6—H6C	109.00
N3—C2—C3	112.0 (2)	H6B—C6—H6A	109.00
C6—C2—C3	120.4 (2)	C2—C6—H6B	109.00
O4—C7—N4	124.0 (2)	H6B—C6—H6C	110.00
O4—C7—N5	118.5 (2)	H6A—C6—H6C	109.00
N4—C7—N5	117.5 (2)	C2—C6—H6A	109.00
O5—C9—O6	122.6 (2)	C10—C11—H11A	109.00
O5—C9—C8	125.1 (2)	C10—C11—H11B	109.00
O6—C9—C8	112.3 (2)	H11A—C11—H11B	109.00
O2—C3—O3	123.1 (2)	H11A—C11—H11C	109.00
O2—C3—C2	125.5 (2)	H11B—C11—H11C	109.00
O3—C3—C2	111.4 (2)	C10—C11—H11C	110.00
O6—C10—C11	107.2 (2)	O6—C10—H10A	110.00
O3—C4—C5	107.8 (2)	C11—C10—H10A	110.00
H7A—O7—H7B	114.00	C11—C10—H10B	110.00
C1—N1—H1N2	120.3 (18)	O6—C10—H10B	110.00
H1N1—N1—H1N2	123 (2)	C8—C12—H12B	109.00
C1—N1—H1N1	116.8 (16)	C8—C12—H12C	109.00

C1—N2—H2N	117.1 (16)	C8—C12—H12A	109.00
N3—N2—H2N	123.8 (16)	H12A—C12—H12C	109.00
C7—N5—H5N	118.2 (16)	H12B—C12—H12C	109.00
N6—N5—H5N	122.9 (16)	H12A—C12—H12B	110.00
C4—O3—C3—O2	−1.3 (4)	N6—N5—C7—O4	176.9 (2)
C4—O3—C3—C2	179.6 (2)	N6—N5—C7—N4	−3.4 (4)
C3—O3—C4—C5	177.3 (2)	N5—N6—C8—C9	179.6 (2)
C10—O6—C9—C8	−179.0 (2)	N5—N6—C8—C12	−0.5 (4)
C9—O6—C10—C11	180.0 (3)	N3—C2—C3—O2	6.4 (4)
C10—O6—C9—O5	0.8 (4)	C6—C2—C3—O2	−173.1 (3)
C1—N2—N3—C2	−178.6 (2)	C6—C2—C3—O3	6.0 (3)
N3—N2—C1—O1	−178.2 (2)	N3—C2—C3—O3	−174.5 (2)
N3—N2—C1—N1	2.0 (4)	N6—C8—C9—O5	1.0 (4)
N2—N3—C2—C6	0.4 (4)	N6—C8—C9—O6	−179.1 (2)
N2—N3—C2—C3	−179.1 (2)	C12—C8—C9—O5	−178.9 (3)
C7—N5—N6—C8	178.1 (2)	C12—C8—C9—O6	1.0 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*N*1···O1	0.85 (3)	2.19 (3)	3.030 (3)	166 (3)
N1—H1*N*1···O4	0.86 (3)	2.14 (3)	2.989 (3)	169 (3)
N2—H2*N*···O4^{i}	0.84 (2)	2.09 (2)	2.920 (3)	169 (2)
N4—H4*N*2···O7^{iv}	0.92 (3)	2.05 (3)	2.950 (3)	169 (3)
N1—H1*N*2···N3	0.88 (3)	2.31 (3)	2.656 (3)	103.5 (18)
N1—H1*N*2···O7	0.88 (3)	2.10 (3)	2.955 (3)	163 (3)
N5—H5*N*···O1^{iii}	0.84 (2)	2.11 (2)	2.935 (3)	167 (2)
O7—H7*A*···O2	0.92	1.92	2.809 (3)	163
O7—H7*B*···O5^{v}	0.88	2.01	2.826 (3)	153
C6—H6*C*···O4^{i}	0.96	2.47	3.397 (3)	162
C6—H6*C*···N2	0.96	2.50	2.879 (3)	103
C12—H12*C*···O6	0.96	2.36	2.770 (3)	105

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