IUCrData

ISSN 2414-3146

L-Methionine–succinic acid (2/1)

M. Nageshwari, S. Kumaresan, M. Lydia Caroline,* G. Mani, C. Rathika Thaya Kumari, S. Sudha and P. Jayaprakash

PG and Research Department of Physics, Arignar Anna Government Arts College, Cheyyar 604 407, Tamil Nadu, India. *Correspondence e-mail: lydiacaroline2006@yahoo.co.in

Received 19 December 2015
Accepted 21 December 2015

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

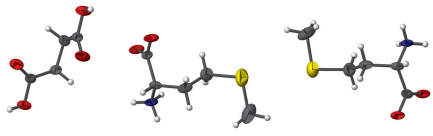
Keywords: crystal structure; L-methionine; succinic acid; hydrogen bonding.

CCDC reference: 1443737

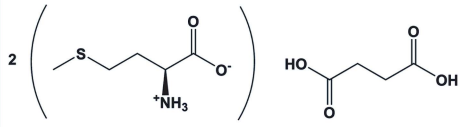
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $2C_5H_{11}NO_2S\cdot C_4H_6O_4$, comprises two crystallographically independent methionine residues, which exist in the zwitterionic form, and a neutral succinic acid molecule. Both methionine residues have a *gauche*-I conformation. In the crystal, the various components are linked *via* O—H···O, N—H···O and C—H···O hydrogen bonds forming slabs parallel to the *ab* plane

3D view



Chemical scheme



Structure description

Methionine is a sulfur-containing amino acid which is essential for normal metabolism, growth and maintenance of body tissues (Sridhar *et al.*, 2002). In conjunction with our ongoing work on nonlinear optical crystals, among the 20 naturally occurring amino acids we have focused our interest towars methionine, which is one of the essential amino acids for humans. In this paper, the crystal structure of the product of the reaction of L-methionine with succinic acid is reported.

The molecular structure of the title compound is represented in Fig. 1. The asymmetric unit contains two methionine residues and a neutral succinic acid molecule. Both methionine residues exhibit a *gauche* I conformation. The bond distances C5—O6, C5—O5, C10—O7 and C10—O8 are 1.244 (9), 1.248 (9), 1.232 (9) and 1.260 (9) Å, respectively, indicating deprotonated carboxylate groups in each methionine residue. This unsymmetrical unit has bond angles O5—C5—O6 and O8—C10—O7 of 125.6 (7) and 124.7 (7) °, respectively. The backbone torsion angles Ψ1 for the central methionine of O5—C5—C6—N1 and O6—C5—C6—N1 are 4.8 (9) and −176.1 (6)°, respectively. For the end methionine residue, the backbone torsion angles Ψ1 of O7—C10—C11—N2 and O8—C10—C11—N2 are 5.8 (9) and −174.4 (6) °, respectively. The side-chain conformation for both methionine residues is *gauche* I *trans gauche* I. All possible rotational

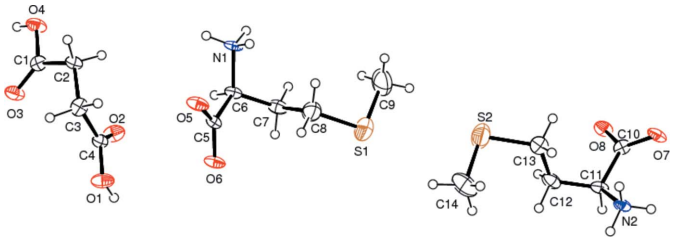


Figure 1
The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 40% probability level.

isomers are found to exist in the methionine residues (Pandiarajan *et al.*, 2002). In both the methionine residues, the straight side-chain conformation angles $\chi1$ are in the *gauche* I form [70.9 (9) and 67.3 (9)°], $\chi2$ are *trans* [179.5 (6) and 177.6 (6)°] and $\chi3$ are again *gauche* I [71.9 (9) and 72.1 (9)°].

In the crystal, the various components are linked *via* O—H···O, N—H···O and C—H···O hydrogen bonds, forming slabs parallel to the *ab* plane (Table 1 and Fig. 2). There are no direct hydrogen-bonding interactions between the succinic acid molecules. The methionine residues are interlinked through the succinic acid molecules. The crystal packing may be visualized as hydrogen-bonded triple layers, a characteristic feature of α-amino acids with hydrocarbon side chains, stacked in such a way that the hydrophobic side chains of the methionine molecules are facing close to each other with respect to succinic acid (Fig. 2).

Synthesis and crystallization

Colourless transparent single crystals of the title compound were obtained by slow evaporation of an aqueous solution of L-methionine and succinic acid, in a stoichiometric ratio of 2:1, over a period of 20 days.

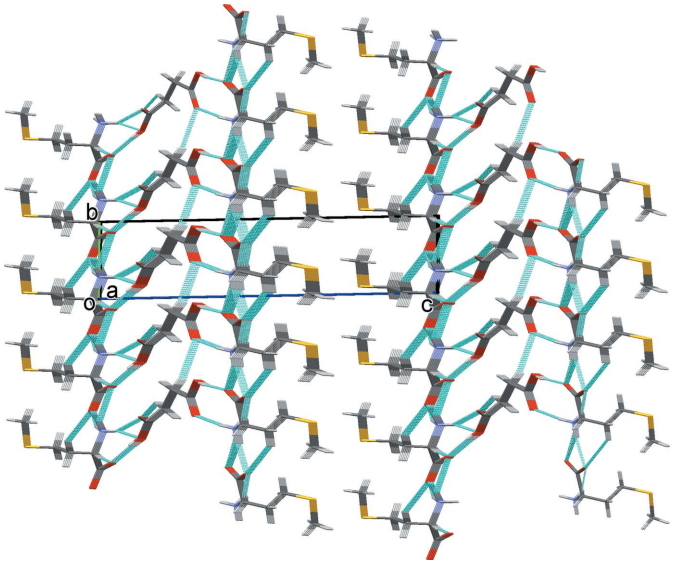


Figure 2
The crystal packing of the title compound, viewed along the *a* axis. The hydrogen bonds are shown as dashed lines (see Table 1 for details).

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O5^{i}	0.82	1.83	2.639 (7)	168
O4—H4···O7^{ii}	0.82	1.84	2.647 (7)	169
N1—H1*C*···O1^{iii}	0.90 (3)	2.59 (8)	3.133 (9)	120 (7)
N1—H1*C*···O2^{iv}	0.90 (3)	2.09 (7)	2.842 (8)	140 (9)
N1—H1*A*···O5^{iii}	0.90 (3)	2.47 (8)	3.168 (8)	135 (9)
N1—H1*A*···O6^{iii}	0.90 (3)	2.01 (4)	2.866 (8)	160 (10)
N1—H1*B*···O6^{iv}	0.90 (3)	2.03 (5)	2.897 (8)	161 (10)
N2—H2*C*···O3^{v}	0.89	2.07	2.849 (8)	146
N2—H2*D*···O8^{vi}	0.89	2.07	2.904 (8)	156
N2—H2*E*···O7^{vii}	0.89	2.45	3.169 (8)	139
N2—H2*E*···O8^{vii}	0.89	2.01	2.875 (8)	163
C6—H6···O5^{viii}	0.98	2.26	3.206 (9)	162
C11—H11···O7^{i}	0.98	2.28	3.210 (9)	159
C12—H12*B*···O8^{vii}	0.97	2.65	3.415 (10)	136

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

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_5H_{11}NO_2S{\cdot}C_4H_6O_4$
M_r	416.50
Crystal system, space group	Triclinic, *P*1
Temperature (K)	293
a, *b*, *c* (Å)	5.0283 (4), 5.0580 (4), 20.8394 (18)
α, β, γ (°)	86.645 (2), 83.338 (3), 68.908 (5)
V (Å^3)	491.08 (7)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.31
Crystal size (mm)	0.35 × 0.30 × 0.25
Data collection	
Diffractometer	Bruker Kappa APEXII CCD diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.873, 0.956
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8433, 3428, 3251
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.063, 0.171, 1.11
No. of reflections	3428
No. of parameters	244
No. of restraints	9
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.38
Absolute structure	Flack *x* determined using 1325 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.06 (4)

Computer programs: *APEX2* (Bruker, 2004), *SAINT* (Bruker, 2004), *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1994), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008).

Acknowledgements

The authors thank the Sophisticated Analytical Instruments facility, Indian Institute of Technology IITM, Chennai, for providing scientific support in solving the crystal structure. The authors personally thank Professor Subramanian (Retired) Professor of Chemistry, Pachayappa's College, Kanchipuram, Tamilnadu, for his valuable suggestions.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bruker (2004). *APEX2*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o882–o884.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Sridhar, B., Srinivasan, N., Dalhus, B. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o779–o781.

full crystallographic data

IUCrData (2016). **1**, x152459 [doi:10.1107/S2414314615024591]

L-Methionine–succinic acid (2/1)

M. Nageshwari, S. Kumaresan, M. Lydia Caroline, G. Mani, C. Rathika Thaya Kumari, S. Sudha and P. Jayaprakash

L-Methionine–succinic acid (2/1)

Crystal data

$2C_5H_{11}NO_2S·C_4H_6O_4$
M_r = 416.50
Triclinic, $P\overline{1}$
a = 5.0283 (4) Å
b = 5.0580 (4) Å
c = 20.8394 (18) Å
α = 86.645 (2)°
β = 83.338 (3)°
γ = 68.908 (5)°
V = 491.08 (7) Å^3
Z = 1
$F(000)$ = 222
D_x = 1.408 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5997 reflections
θ = 3.0–28.3°
μ = 0.31 mm^{-1}
T = 293 K
Block, colourless
0.35 × 0.30 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.873, T_{max} = 0.956
8433 measured reflections
3428 independent reflections
3251 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 26.0°, θ_{min} = 3.0°
h = −6→6
k = −6→5
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.171
S = 1.11
3428 reflections
244 parameters
9 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 1.4388P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Absolute structure: Flack x determined using 1325 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.06 (4)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0929 (15)	−0.3017 (17)	1.2684 (3)	0.0267 (16)
C2	0.0926 (16)	−0.1994 (15)	1.2208 (4)	0.0278 (16)
H2A	0.1576	−0.0710	1.2419	0.033*
H2B	−0.0187	−0.0941	1.1866	0.033*
C3	0.3501 (15)	−0.4389 (17)	1.1917 (4)	0.0294 (17)
H3A	0.4878	−0.3610	1.1701	0.035*
H3B	0.4404	−0.5647	1.2262	0.035*
C4	0.2765 (16)	−0.6065 (15)	1.1445 (3)	0.0256 (15)
C5	0.2712 (15)	−0.2155 (15)	0.9996 (3)	0.0238 (15)
C6	−0.0208 (14)	−0.0051 (14)	0.9834 (4)	0.0239 (15)
H6	−0.1672	−0.0747	1.0051	0.029*
C7	−0.0529 (17)	0.0129 (17)	0.9119 (4)	0.0340 (18)
H7A	−0.0575	−0.1664	0.8990	0.041*
H7B	−0.2363	0.1576	0.9048	0.041*
C8	0.177 (2)	0.079 (2)	0.8687 (4)	0.050 (2)
H8A	0.3612	−0.0645	0.8758	0.060*
H8B	0.1809	0.2597	0.8811	0.060*
C9	−0.165 (3)	0.420 (3)	0.7771 (6)	0.082 (4)
H9A	−0.2084	0.4513	0.7330	0.122*
H9B	−0.3287	0.4079	0.8041	0.122*
H9C	−0.1182	0.5748	0.7906	0.122*
C10	0.2140 (15)	0.6224 (16)	0.4123 (4)	0.0259 (16)
C11	0.4113 (15)	0.3242 (15)	0.4278 (4)	0.0254 (15)
H11	0.3531	0.1939	0.4047	0.030*
C12	0.3860 (17)	0.2466 (18)	0.4989 (4)	0.0353 (18)
H12A	0.1932	0.2486	0.5112	0.042*
H12B	0.5166	0.0540	0.5049	0.042*
C13	0.447 (2)	0.433 (2)	0.5437 (4)	0.045 (2)
H13A	0.3217	0.6271	0.5365	0.054*
H13B	0.6424	0.4248	0.5327	0.054*
C14	0.709 (3)	0.027 (3)	0.6336 (7)	0.072 (4)
H14A	0.7119	−0.0447	0.6773	0.108*
H14B	0.6967	−0.1123	0.6057	0.108*
H14C	0.8805	0.0655	0.6206	0.108*
N1	−0.0777 (13)	0.2796 (12)	1.0094 (3)	0.0280 (14)
N2	0.7110 (12)	0.2804 (13)	0.4033 (3)	0.0263 (13)
H2C	0.7204	0.3274	0.3615	0.039*
H2D	0.7744	0.3884	0.4250	0.039*
H2E	0.8190	0.0991	0.4086	0.039*

O1	0.4981 (11)	−0.8243 (12)	1.1218 (3)	0.0378 (14)
H1	0.4469	−0.9096	1.0963	0.057*
O2	0.0410 (11)	−0.5487 (13)	1.1270 (3)	0.0389 (14)
O3	−0.0496 (12)	−0.5422 (12)	1.2855 (3)	0.0370 (13)
O4	−0.3294 (11)	−0.0864 (11)	1.2910 (3)	0.0364 (13)
H4	−0.4281	−0.1485	1.3172	0.055*
O5	0.4115 (11)	−0.1349 (11)	1.0347 (3)	0.0343 (13)
O6	0.3459 (11)	−0.4561 (11)	0.9767 (3)	0.0338 (12)
O7	0.3106 (11)	0.7815 (11)	0.3784 (3)	0.0332 (13)
O8	−0.0432 (11)	0.6879 (11)	0.4360 (3)	0.0338 (12)
S1	0.1337 (7)	0.0957 (6)	0.78374 (14)	0.0737 (10)
S2	0.4020 (6)	0.3478 (6)	0.62834 (14)	0.0685 (9)
H1C	−0.08 (2)	0.28 (2)	1.0528 (13)	0.082*
H1A	−0.245 (11)	0.40 (2)	0.997 (4)	0.082*
H1B	0.065 (15)	0.34 (2)	0.992 (4)	0.082*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.019 (4)	0.031 (5)	0.030 (4)	−0.009 (3)	−0.005 (3)	−0.004 (3)
C2	0.027 (4)	0.019 (4)	0.037 (4)	−0.008 (3)	−0.003 (3)	−0.001 (3)
C3	0.020 (4)	0.040 (5)	0.034 (4)	−0.017 (4)	−0.001 (3)	−0.001 (3)
C4	0.023 (4)	0.022 (4)	0.032 (4)	−0.008 (3)	0.000 (3)	−0.001 (3)
C5	0.021 (4)	0.017 (4)	0.033 (4)	−0.006 (3)	−0.003 (3)	0.003 (3)
C6	0.015 (3)	0.016 (4)	0.041 (4)	−0.007 (3)	0.000 (3)	−0.003 (3)
C7	0.028 (4)	0.023 (4)	0.052 (5)	−0.008 (3)	−0.015 (3)	−0.004 (3)
C8	0.051 (6)	0.051 (6)	0.041 (5)	−0.009 (5)	−0.006 (4)	−0.001 (4)
C9	0.109 (12)	0.081 (10)	0.056 (8)	−0.032 (9)	−0.031 (7)	0.019 (6)
C10	0.015 (3)	0.033 (4)	0.032 (4)	−0.009 (3)	−0.004 (3)	−0.007 (3)
C11	0.015 (3)	0.018 (4)	0.045 (4)	−0.007 (3)	−0.002 (3)	−0.005 (3)
C12	0.022 (4)	0.025 (4)	0.054 (5)	−0.005 (3)	−0.001 (3)	0.005 (3)
C13	0.055 (6)	0.038 (5)	0.040 (5)	−0.014 (5)	−0.003 (4)	0.000 (4)
C14	0.065 (8)	0.049 (7)	0.090 (9)	−0.001 (6)	−0.031 (7)	0.022 (6)
N1	0.025 (3)	0.010 (3)	0.045 (4)	0.000 (3)	−0.007 (3)	−0.005 (2)
N2	0.017 (3)	0.017 (3)	0.041 (3)	−0.001 (3)	−0.002 (2)	0.001 (3)
O1	0.023 (3)	0.031 (3)	0.058 (4)	−0.006 (3)	−0.004 (2)	−0.015 (3)
O2	0.020 (3)	0.045 (4)	0.050 (3)	−0.007 (3)	−0.005 (2)	−0.015 (3)
O3	0.034 (3)	0.022 (3)	0.050 (3)	−0.009 (3)	0.008 (3)	−0.001 (2)
O4	0.026 (3)	0.022 (3)	0.055 (4)	−0.005 (3)	0.007 (2)	−0.002 (2)
O5	0.024 (3)	0.020 (3)	0.059 (3)	−0.005 (2)	−0.014 (2)	−0.005 (2)
O6	0.024 (3)	0.017 (3)	0.055 (3)	0.001 (2)	−0.008 (2)	−0.006 (2)
O7	0.022 (3)	0.016 (3)	0.058 (3)	−0.004 (2)	0.000 (2)	0.005 (2)
O8	0.016 (3)	0.028 (3)	0.053 (3)	−0.003 (2)	−0.001 (2)	0.003 (2)
S1	0.098 (2)	0.075 (2)	0.0378 (14)	−0.0181 (19)	−0.0056 (14)	−0.0013 (12)
S2	0.075 (2)	0.080 (2)	0.0399 (14)	−0.0173 (17)	−0.0014 (12)	0.0058 (13)

Geometric parameters (Å, º)

C1—O3	1.196 (9)	C9—H9C	0.9600
C1—O4	1.349 (9)	C10—O7	1.232 (9)
C1—C2	1.480 (10)	C10—O8	1.260 (9)
C2—C3	1.512 (10)	C10—C11	1.518 (10)
C2—H2A	0.9700	C11—N2	1.475 (9)
C2—H2B	0.9700	C11—C12	1.513 (11)
C3—C4	1.494 (10)	C11—H11	0.9800
C3—H3A	0.9700	C12—C13	1.496 (13)
C3—H3B	0.9700	C12—H12A	0.9700
C4—O2	1.208 (9)	C12—H12B	0.9700
C4—O1	1.317 (9)	C13—S2	1.798 (9)
C5—O6	1.244 (9)	C13—H13A	0.9700
C5—O5	1.248 (9)	C13—H13B	0.9700
C5—C6	1.533 (10)	C14—S2	1.801 (12)
C6—N1	1.486 (9)	C14—H14A	0.9600
C6—C7	1.511 (11)	C14—H14B	0.9600
C6—H6	0.9800	C14—H14C	0.9600
C7—C8	1.505 (13)	N1—H1C	0.90 (3)
C7—H7A	0.9700	N1—H1A	0.90 (3)
C7—H7B	0.9700	N1—H1B	0.90 (3)
C8—S1	1.802 (9)	N2—H2C	0.8900
C8—H8A	0.9700	N2—H2D	0.8900
C8—H8B	0.9700	N2—H2E	0.8900
C9—S1	1.793 (15)	O1—H1	0.8200
C9—H9A	0.9600	O4—H4	0.8200
C9—H9B	0.9600		
O3—C1—O4	122.1 (7)	H9B—C9—H9C	109.5
O3—C1—C2	126.5 (7)	O7—C10—O8	124.7 (7)
O4—C1—C2	111.4 (7)	O7—C10—C11	119.5 (6)
C1—C2—C3	112.4 (6)	O8—C10—C11	115.8 (6)
C1—C2—H2A	109.1	N2—C11—C12	111.2 (6)
C3—C2—H2A	109.1	N2—C11—C10	111.1 (6)
C1—C2—H2B	109.1	C12—C11—C10	113.1 (6)
C3—C2—H2B	109.1	N2—C11—H11	107.1
H2A—C2—H2B	107.9	C12—C11—H11	107.1
C4—C3—C2	113.2 (6)	C10—C11—H11	107.1
C4—C3—H3A	108.9	C13—C12—C11	115.9 (7)
C2—C3—H3A	108.9	C13—C12—H12A	108.3
C4—C3—H3B	108.9	C11—C12—H12A	108.3
C2—C3—H3B	108.9	C13—C12—H12B	108.3
H3A—C3—H3B	107.8	C11—C12—H12B	108.3
O2—C4—O1	122.2 (7)	H12A—C12—H12B	107.4
O2—C4—C3	124.6 (7)	C12—C13—S2	115.5 (6)
O1—C4—C3	113.2 (6)	C12—C13—H13A	108.4
O6—C5—O5	125.6 (7)	S2—C13—H13A	108.4

O6—C5—C6	116.1 (6)	C12—C13—H13B	108.4
O5—C5—C6	118.3 (6)	S2—C13—H13B	108.4
N1—C6—C7	111.0 (6)	H13A—C13—H13B	107.5
N1—C6—C5	111.2 (6)	S2—C14—H14A	109.5
C7—C6—C5	112.6 (6)	S2—C14—H14B	109.5
N1—C6—H6	107.2	H14A—C14—H14B	109.5
C7—C6—H6	107.2	S2—C14—H14C	109.5
C5—C6—H6	107.2	H14A—C14—H14C	109.5
C8—C7—C6	115.7 (6)	H14B—C14—H14C	109.5
C8—C7—H7A	108.4	C6—N1—H1C	112 (7)
C6—C7—H7A	108.4	C6—N1—H1A	109 (8)
C8—C7—H7B	108.4	H1C—N1—H1A	109 (4)
C6—C7—H7B	108.4	C6—N1—H1B	107 (7)
H7A—C7—H7B	107.4	H1C—N1—H1B	110 (4)
C7—C8—S1	114.5 (7)	H1A—N1—H1B	110 (4)
C7—C8—H8A	108.6	C11—N2—H2C	109.5
S1—C8—H8A	108.6	C11—N2—H2D	109.5
C7—C8—H8B	108.6	H2C—N2—H2D	109.5
S1—C8—H8B	108.6	C11—N2—H2E	109.5
H8A—C8—H8B	107.6	H2C—N2—H2E	109.5
S1—C9—H9A	109.5	H2D—N2—H2E	109.5
S1—C9—H9B	109.5	C4—O1—H1	109.5
H9A—C9—H9B	109.5	C1—O4—H4	109.5
S1—C9—H9C	109.5	C9—S1—C8	102.1 (5)
H9A—C9—H9C	109.5	C13—S2—C14	100.4 (6)

O3—C1—C2—C3	2.7 (10)	C6—C7—C8—S1	179.5 (6)
O4—C1—C2—C3	−176.5 (6)	O7—C10—C11—N2	5.8 (9)
C1—C2—C3—C4	73.3 (8)	O8—C10—C11—N2	−174.4 (6)
C2—C3—C4—O2	5.1 (11)	O7—C10—C11—C12	131.6 (7)
C2—C3—C4—O1	−176.5 (6)	O8—C10—C11—C12	−48.6 (8)
O6—C5—C6—N1	−176.1 (6)	N2—C11—C12—C13	67.3 (9)
O5—C5—C6—N1	4.8 (9)	C10—C11—C12—C13	−58.5 (9)
O6—C5—C6—C7	−50.7 (9)	C11—C12—C13—S2	177.6 (6)
O5—C5—C6—C7	130.2 (7)	C7—C8—S1—C9	71.9 (9)
N1—C6—C7—C8	70.9 (9)	C12—C13—S2—C14	72.1 (9)
C5—C6—C7—C8	−54.5 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O5^{i}	0.82	1.83	2.639 (7)	168
O4—H4···O7^{ii}	0.82	1.84	2.647 (7)	169
N1—H1*C*···O1^{iii}	0.90 (3)	2.59 (8)	3.133 (9)	120 (7)
N1—H1*C*···O2^{iv}	0.90 (3)	2.09 (7)	2.842 (8)	140 (9)
N1—H1*A*···O5^{iii}	0.90 (3)	2.47 (8)	3.168 (8)	135 (9)
N1—H1*A*···O6^{iii}	0.90 (3)	2.01 (4)	2.866 (8)	160 (10)
N1—H1*B*···O6^{iv}	0.90 (3)	2.03 (5)	2.897 (8)	161 (10)

N2—H2*C*···O3^{v}	0.89	2.07	2.849 (8)	146
N2—H2*D*···O8^{vi}	0.89	2.07	2.904 (8)	156
N2—H2*E*···O7^{vii}	0.89	2.45	3.169 (8)	139
N2—H2*E*···O8^{vii}	0.89	2.01	2.875 (8)	163
C6—H6···O5^{viii}	0.98	2.26	3.206 (9)	162
C11—H11···O7^{i}	0.98	2.28	3.210 (9)	159
C12—H12*B*···O8^{vii}	0.97	2.65	3.415 (10)	136

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