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Crystal structures of the isomeric dipeptides L-glycyl-L-methionine and L-methionyl-L-glycine

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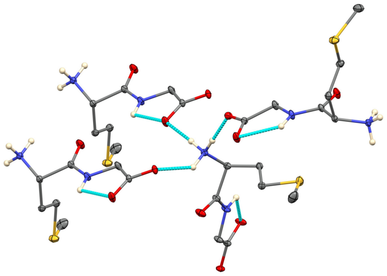
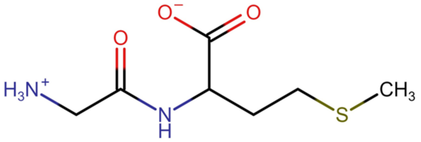
The oxidation of methionyl peptides can contribute to increased biological (oxidative) stress and development of various inflammatory diseases. The conformation of peptides has an important role in the mechanism of oxidation and the intermediates formed in the reaction. Herein, the crystal structures of the isomeric dipeptides Gly-Met (Gly = glycine and Met = methionine) and Met-Gly, both $C_7H_{14}N_2O_3S$, are reported. Both molecules exist in the solid state as zwitterions with nominal proton transfer from the carboxylic acid to the primary amine group. The Gly-Met molecule has an extended backbone structure, while Met-Gly has two nearly planar regions kinked at the C atom bearing the NH_3 group. In the crystals, both structures form extensive three-dimensional hydrogen-bonding networks *via* N—H···O and bifurcated N—H···(O,O) hydrogen bonds having N···O distances in the range 2.6619 (13)–2.8513 (13) Å for Gly-Met and 2.6273 (8)–3.1465 (8) Å for Met-Gly.

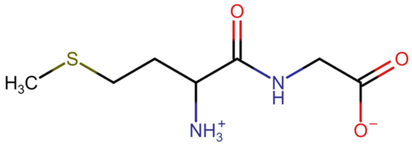


1. Chemical context

Methionine and methionyl peptides play an important role in protein oxidation. The sulfur atom in methionine can easily be oxidized by free radicals or oxidants and lead to sulfur radical cations (Bobrowski & Holcman, 1989) or a corresponding sulfoxide (Schöneich, 2005). The formation of reactive radical cations is responsible for methionyl protein damage and misconformation, which has been implicated in numerous inflammatory (Vogt, 1995) and age-related diseases (Schöneich, 2005; Stadtman *et al.*, 2005).



Gly-Met



Met-Gly

Gly-Met (Gly = glycine, Met = methionine) and its reverse sequence, Met-Gly, are two simple dipeptides. It has been shown that the position of methionine with respect to the N-terminus of the peptide determines the mechanism of

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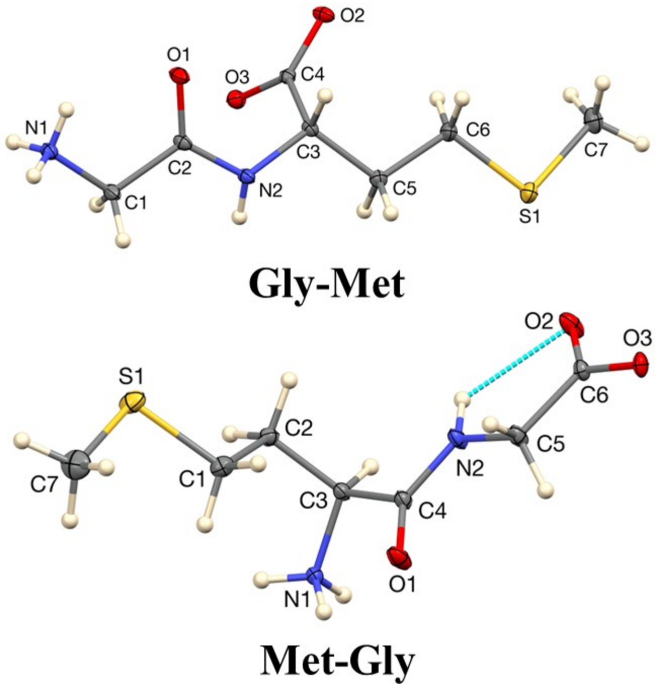

Figure 1
The molecular structures of Gly-Met and Met-Gly showing 50% displacement ellipsoids.

oxidation of methionyl peptides. For instance, in photosensitized oxidation reactions, substantial amounts of radical cations stabilized with sulfur–nitrogen (S∴N) three-electron bonded species were observed with Met-Gly, while similar stabilization of the radical cations was not observed with Gly-Met (Pedzinski *et al.*, 2009). In collision-induced radical dissociation, Gly-Met leads to the loss of a $CH_3-S-CH{=}CH_2$ fragment from the peptide, while such dissociation in Met-Gly leads to the loss of a $CH_3S^{\bullet}$ (Lau *et al.*, 2013) radical. Thus, the difference in methionine position leads to quite different reaction intermediates, which may eventually affect the stability of the peptide and its biological function.

The oxidation of methionine peptides is determined by several factors, including peptide structure, the position of methionine within the sequence, neighboring groups to methionine, nature of the oxidants, and solvent properties. The conformation of the peptide is also an important factor that needs to be considered to understand the mechanism of oxidation. Peptides can exist in either cationic, zwitterionic, or anionic conformations, depending on the solvent and the pH. The present report describes the zwitterionic structures of Gly-Met and Met-Gly dipeptides. We believe that some of the differences observed in the literature related to methionyl peptide oxidations could be attributed to the conformation of the peptide in solution.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H11N\cdots O3^{i}$	0.83 (2)	2.15 (2)	2.8513 (13)	143.0 (18)
$N1-H11N\cdots O1$	0.83 (2)	2.15 (2)	2.6619 (13)	120.1 (16)
$N1-H12N\cdots O2^{ii}$	0.886 (19)	1.850 (19)	2.7275 (12)	170.7 (18)
$N1-H13N\cdots O3^{iii}$	0.849 (19)	1.86 (2)	2.7006 (13)	168 (2)
$N2-H2N\cdots O2^{iv}$	0.832 (19)	2.000 (19)	2.8225 (12)	170.0 (18)

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

Table 2
Hydrogen-bond geometry (Å, °) for Met-Gly.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H11N\cdots O2^{i}$	0.885 (14)	1.854 (14)	2.7290 (8)	169.5 (13)
$N1-H11N\cdots O3^{i}$	0.885 (14)	2.593 (15)	3.1465 (8)	121.4 (11)
$N1-H12N\cdots O3^{ii}$	0.896 (13)	1.857 (13)	2.7531 (7)	179.6 (14)
$N1-H13N\cdots O3^{iii}$	0.907 (14)	2.015 (14)	2.7529 (8)	137.5 (11)
$N1-H13N\cdots O1$	0.907 (14)	2.211 (13)	2.6940 (8)	112.7 (10)
$N2-H2N\cdots O2$	0.879 (15)	2.185 (13)	2.6273 (8)	110.6 (10)

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

2. Structural commentary

Both of the dipeptides are in their zwitterionic forms in the solid state (Fig. 1). The amide N1 atom of both Gly-Met and Met-Gly is in the protonated NH_3^+ form, and the C6/O2/O3 carboxylic groups are in their deprotonated $(COO)^-$ forms, as evidenced by the C—O distances of 1.2598 (13) and 1.2546 (13) Å in Gly-Met and 1.2534 (9) and 1.2635 (8) Å in Met-Gly. The C—NH_3 distance is 1.4809 (14) Å in Gly-Met and 1.4855 (8) in Met-Gly. The backbone of the Gly-Met molecule is extended, with its six torsion angle magnitudes in the range 163.44 (9)–177.94 (8)°. Thus, the ten atoms of the chain are close to coplanar with a mean deviation of 0.091 Å. The backbone of the Met-Gly molecule is substantially kinked at C3. The eight-atom segment containing the carboxylate group is planar to within a mean deviation of 0.056 Å, and the five-atom segment containing the S atom is planar to within a mean deviation of 0.086 Å. These two planes intersect at C3, forming a dihedral angle of 70.502 (13)°. The absolute configurations of both molecules were confirmed from their refined Flack parameters (Parsons *et al.*, 2013), with values of 0.02 (2) for Gly-Met and 0.011 (11) for Met-Gly.

3. Supramolecular features

Intermolecular interactions in both structures are dominated by N—H⋯O hydrogen bonds, some of which are bifurcated. In Gly-Met (Table 1), the NH_3^+ group donates hydrogen bonds to three separate molecules, and the N—H group donates to a fourth (Fig. 2), forming a complex three-dimensional array of hydrogen bonds. Graph sets (Etter *et al.*, 1990) include $C_1^1(5)$ and $C_1^1(8)$ chains and $R_4^4(22)$ loops. In Met-Gly (Table 2), the NH_3^+ group also donates hydrogen bonds to three different molecules (Fig. 3), but the N—H group does not participate in intermolecular interactions and makes a very non-linear [$N-H\cdots O = 110.6\ (10)°$] intramolecular contact to an O atom of the carboxylate group. Nevertheless, the hydrogen-bonding array is three-dimensional, and graph sets include $C_1^1(8)$ chains, $C_2^2(6)$ chains and $R_4^4(22)$ loops.

Table 3
Experimental details.

	Gly-Met	Met-Gly
Crystal data		
Chemical formula	$C_7H_{14}N_2O_3S$	$C_7H_{14}N_2O_3S$
M_r	206.26	206.26
Crystal system, space group	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	90	90
a, b, c (Å)	6.2517 (2), 5.4935 (2), 14.5686 (6)	5.2521 (3), 11.4126 (7), 16.5403 (10)
α, β, γ (°)	90, 91.147 (4), 90	90, 90, 90
V (Å^3)	500.24 (3)	991.43 (10)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.30	0.31
Crystal size (mm)	0.38 × 0.29 × 0.03	0.25 × 0.24 × 0.17
Data collection		
Diffractometer	Bruker Kappa APEXII DUO CCD	Bruker Kappa APEXII DUO CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.836, 0.991	0.872, 0.950
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11393, 5922, 5356	33593, 6231, 5939
R_{int}	0.026	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.909	0.909
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.079, 1.04	0.023, 0.061, 1.06
No. of reflections	5922	6231
No. of parameters	131	131
No. of restraints	1	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.30	0.44, −0.20
Absolute structure	Flack x determined using 2141 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ Parsons *et al.* (2013)	Flack x determined using 2494 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ Parsons *et al.* (2013)
Absolute structure parameter	0.02 (2)	0.011 (11)

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/1* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.45, Update 1, March 2024; Groom *et al.*, 2016) revealed that no crystal structures were reported for either Gly-Met or Met-Gly. Other dipeptides containing methionine have been reported, including L-Ala-L-Met hemihydrate (Gorbitz, 2003), DL-Ala-LD-Met (Jha *et al.*, 2020), L-Pro-L-Met monohydrate (Padmanabhan & Yadava, 1983), L-Met-L-Met (Stenkamp & Jensen, 1975), L-Met-L-Ala (Gorbitz, 2000), and L-Met-L-Ser (Gorbitz *et al.*, 2006).

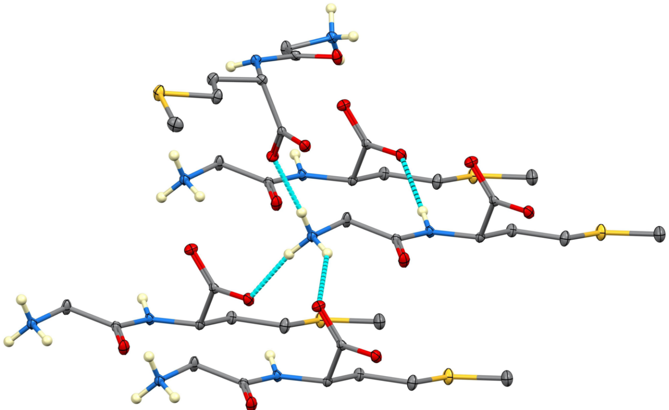

Figure 2
Hydrogen bonding in Gly-Met. H atoms on C are not shown.

5. Synthesis and crystallization

The dipeptides Gly-Met and Met-Gly were obtained commercially (Chem-impex International Inc., Wood Dale, IL, USA). A supersaturated solution of each dipeptide was prepared in a small test tube by mixing the compound with warm methanol. Approximately 100 mg of dipeptide was added to 10 ml of methanol and additional solvent was added

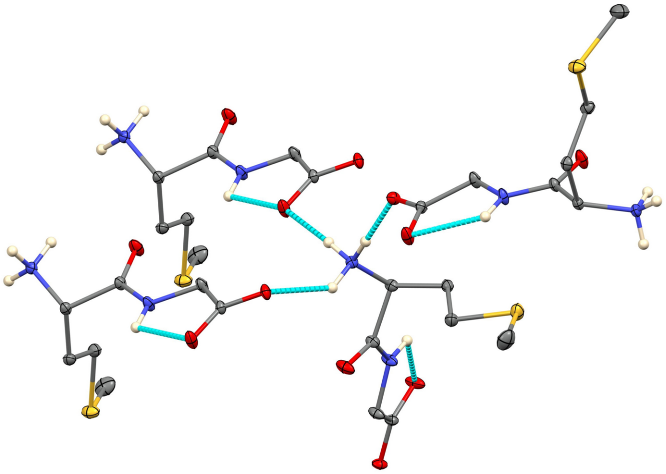

Figure 3
Hydrogen bonding in Met-Gly. H atoms on C are not shown.

slowly in small increments with agitation and keeping the test tube at 333 K in a water bath. The solutions were allowed to cool and left undisturbed at room temperature over two weeks for slow evaporation and crystallization to yield colorless plates of Gly-Met and large colorless needles of Met-Gly.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were located in difference maps and those on carbon were treated as riding in geometrically idealized positions with C—H distances = 1.00 Å for R_3CH, 0.99 Å for CH_2 and 0.98 Å for methyl. $U_{\rm iso}$(H) values were assigned as $1.2U_{\rm eq}$ for the attached C atom ($1.5U_{\rm eq}$ for methyl). The positions of the H atoms attached to N atoms were refined. Their $U_{\rm iso}$ values were assigned as $1.2U_{\rm eq}$ for the NH groups and $1.5U_{\rm eq}$ for NH_3.

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Computing details

L-Glycyl-*L*-methionine (Gly-Met)

Crystal data

$C_7H_{14}N_2O_3S$
$M_r = 206.26$
Monoclinic, $P2_1$
$a = 6.2517$ (2) Å
$b = 5.4935$ (2) Å
$c = 14.5686$ (6) Å
$\beta = 91.147$ (4)°
$V = 500.24$ (3) Å^3
$Z = 2$

$F(000) = 220$
$D_x = 1.369$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5067 reflections
$\theta = 2.8$–40.1°
$\mu = 0.30$ mm^{-1}
$T = 90$ K
Plate, colourless
0.38 × 0.29 × 0.03 mm

Data collection

Bruker Kappa APEXII DUO CCD diffractometer
Radiation source: fine-focus sealed tube
TRIUMPH curved graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.836$, $T_{max} = 0.991$

11393 measured reflections
5922 independent reflections
5356 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 40.3°$, $\theta_{min} = 2.8°$
$h = -9 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.079$
$S = 1.04$
5922 reflections
131 parameters
1 restraint
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Absolute structure: Flack x determined using 2141 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ Parsons *et al.* (2013)
Absolute structure parameter: 0.02 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
S1	−0.20146 (4)	0.44474 (6)	0.42848 (2)	0.01468 (6)
O1	0.69310 (13)	0.51962 (16)	0.16278 (6)	0.01361 (15)
O2	0.19251 (13)	0.15688 (15)	0.17287 (6)	0.01189 (14)
O3	0.17853 (13)	0.50896 (16)	0.09597 (6)	0.01188 (13)
N1	0.87880 (15)	0.89936 (16)	0.08355 (7)	0.00999 (15)
H11N	0.913 (3)	0.757 (4)	0.0948 (13)	0.015*
H12N	0.981 (3)	0.994 (4)	0.1072 (12)	0.015*
H13N	0.865 (3)	0.912 (4)	0.0257 (13)	0.015*
N2	0.42247 (14)	0.73584 (17)	0.22578 (7)	0.00962 (14)
H2N	0.353 (3)	0.863 (4)	0.2171 (13)	0.012*
C1	0.67091 (16)	0.9440 (2)	0.12752 (8)	0.01317 (16)
H1D	0.563279	0.995080	0.080609	0.016*
H1E	0.686342	1.076254	0.173329	0.016*
C2	0.59716 (16)	0.71258 (19)	0.17425 (7)	0.00938 (15)
C3	0.30874 (16)	0.51654 (19)	0.25172 (7)	0.00890 (15)
H3	0.410296	0.406010	0.285399	0.011*
C4	0.22080 (16)	0.38311 (18)	0.16587 (7)	0.00835 (15)
C5	0.12523 (18)	0.5846 (2)	0.31603 (8)	0.01112 (17)
H5A	0.184307	0.675550	0.369448	0.013*
H5B	0.023082	0.692558	0.282903	0.013*
C6	0.00678 (19)	0.3600 (2)	0.34991 (8)	0.01315 (18)
H6A	0.109333	0.249024	0.381309	0.016*
H6B	−0.057507	0.272165	0.296822	0.016*
C7	−0.3286 (2)	0.1514 (2)	0.43812 (9)	0.0175 (2)
H7A	−0.381335	0.098919	0.377488	0.026*
H7B	−0.448752	0.163281	0.480064	0.026*
H7C	−0.224743	0.032488	0.462053	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01416 (11)	0.01407 (11)	0.01605 (12)	−0.00108 (10)	0.00637 (8)	−0.00091 (10)
O1	0.0117 (3)	0.0077 (3)	0.0216 (4)	0.0011 (3)	0.0036 (3)	0.0016 (3)
O2	0.0114 (3)	0.0072 (3)	0.0170 (4)	−0.0006 (2)	−0.0009 (3)	−0.0006 (3)
O3	0.0144 (3)	0.0112 (3)	0.0100 (3)	0.0016 (3)	−0.0009 (2)	0.0005 (3)
N1	0.0094 (3)	0.0088 (4)	0.0118 (4)	−0.0009 (3)	0.0007 (3)	0.0011 (3)
N2	0.0087 (3)	0.0068 (3)	0.0133 (4)	−0.0008 (3)	0.0007 (3)	0.0006 (3)
C1	0.0119 (4)	0.0079 (3)	0.0199 (4)	0.0005 (4)	0.0050 (3)	0.0024 (4)
C2	0.0085 (4)	0.0074 (3)	0.0121 (4)	−0.0012 (3)	−0.0009 (3)	0.0003 (3)

C3	0.0086 (3)	0.0077 (3)	0.0104 (4)	−0.0009 (3)	0.0001 (3)	0.0014 (3)
C4	0.0068 (3)	0.0076 (3)	0.0107 (4)	0.0006 (3)	0.0011 (3)	−0.0006 (3)
C5	0.0121 (4)	0.0104 (4)	0.0110 (4)	−0.0013 (3)	0.0021 (3)	−0.0007 (3)
C6	0.0141 (4)	0.0113 (4)	0.0142 (4)	−0.0011 (3)	0.0054 (3)	−0.0003 (3)
C7	0.0147 (5)	0.0183 (5)	0.0194 (5)	−0.0046 (4)	0.0030 (4)	0.0025 (4)

Geometric parameters (Å, º)

S1—C7	1.8037 (13)	C1—H1D	0.9900
S1—C6	1.8114 (11)	C1—H1E	0.9900
O1—C2	1.2310 (13)	C3—C4	1.5415 (15)
O2—C4	1.2598 (13)	C3—C5	1.5417 (15)
O3—C4	1.2546 (13)	C3—H3	1.0000
N1—C1	1.4809 (14)	C5—C6	1.5262 (16)
N1—H11N	0.83 (2)	C5—H5A	0.9900
N1—H12N	0.886 (19)	C5—H5B	0.9900
N1—H13N	0.849 (19)	C6—H6A	0.9900
N2—C2	1.3437 (14)	C6—H6B	0.9900
N2—C3	1.4527 (14)	C7—H7A	0.9800
N2—H2N	0.832 (19)	C7—H7B	0.9800
C1—C2	1.5181 (16)	C7—H7C	0.9800

C7—S1—C6	98.22 (6)	C4—C3—H3	108.8
C1—N1—H11N	107.2 (13)	C5—C3—H3	108.8
C1—N1—H12N	111.5 (12)	O3—C4—O2	125.57 (10)
H11N—N1—H12N	107.1 (19)	O3—C4—C3	117.55 (9)
C1—N1—H13N	110.1 (12)	O2—C4—C3	116.86 (9)
H11N—N1—H13N	107.3 (19)	C6—C5—C3	111.85 (9)
H12N—N1—H13N	113.3 (18)	C6—C5—H5A	109.2
C2—N2—C3	118.29 (9)	C3—C5—H5A	109.2
C2—N2—H2N	115.1 (13)	C6—C5—H5B	109.2
C3—N2—H2N	118.5 (13)	C3—C5—H5B	109.2
N1—C1—C2	109.41 (9)	H5A—C5—H5B	107.9
N1—C1—H1D	109.8	C5—C6—S1	110.86 (8)
C2—C1—H1D	109.8	C5—C6—H6A	109.5
N1—C1—H1E	109.8	S1—C6—H6A	109.5
C2—C1—H1E	109.8	C5—C6—H6B	109.5
H1D—C1—H1E	108.2	S1—C6—H6B	109.5
O1—C2—N2	124.15 (10)	H6A—C6—H6B	108.1
O1—C2—C1	120.47 (9)	S1—C7—H7A	109.5
N2—C2—C1	115.37 (9)	S1—C7—H7B	109.5
N2—C3—C4	110.59 (8)	H7A—C7—H7B	109.5
N2—C3—C5	109.33 (9)	S1—C7—H7C	109.5
C4—C3—C5	110.53 (8)	H7A—C7—H7C	109.5
N2—C3—H3	108.8	H7B—C7—H7C	109.5

C3—N2—C2—O1	−15.40 (16)	C5—C3—C4—O3	93.47 (11)
C3—N2—C2—C1	163.44 (9)	N2—C3—C4—O2	153.99 (9)

N1—C1—C2—O1	−8.46 (15)	C5—C3—C4—O2	−84.80 (11)
N1—C1—C2—N2	172.66 (9)	N2—C3—C5—C6	−176.94 (9)
C2—N2—C3—C4	−62.19 (12)	C4—C3—C5—C6	61.10 (12)
C2—N2—C3—C5	175.89 (9)	C3—C5—C6—S1	177.94 (8)
N2—C3—C4—O3	−27.75 (13)	C7—S1—C6—C5	171.26 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11*N*···O3^{i}	0.83 (2)	2.15 (2)	2.8513 (13)	143.0 (18)
N1—H11*N*···O1	0.83 (2)	2.15 (2)	2.6619 (13)	120.1 (16)
N1—H12*N*···O2^{ii}	0.886 (19)	1.850 (19)	2.7275 (12)	170.7 (18)
N1—H13*N*···O3^{iii}	0.849 (19)	1.86 (2)	2.7006 (13)	168 (2)
N2—H2*N*···O2^{iv}	0.832 (19)	2.000 (19)	2.8225 (12)	170.0 (18)

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

L-Methionyl-*L*-glycine (Met-Gly)

Crystal data

$C_7H_{14}N_2O_3S$	D_x = 1.382 Mg m^{-3}
M_r = 206.26	Mo *Kα* radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 9827 reflections
a = 5.2521 (3) Å	θ = 3.0–40.2°
b = 11.4126 (7) Å	μ = 0.31 mm^{-1}
c = 16.5403 (10) Å	*T* = 90 K
V = 991.43 (10) Å^3	Needle fragment, colourless
Z = 4	0.25 × 0.24 × 0.17 mm
F(000) = 440	

Data collection

Bruker Kappa APEXII DUO CCD diffractometer	33593 measured reflections
Radiation source: fine-focus sealed tube	6231 independent reflections
TRIUMPH curved graphite monochromator	5939 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.030
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	θ_{max} = 40.3°, θ_{min} = 2.2°
T_{min} = 0.872, T_{max} = 0.950	$h = -8 \rightarrow 9$
	$k = -20 \rightarrow 20$
	$l = -30 \rightarrow 30$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.0451P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.023	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.061	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −0.20 e Å^{-3}
6231 reflections	Absolute structure: Flack *x* determined using 2494 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ Parsons *et al.* (2013)
131 parameters	Absolute structure parameter: 0.011 (11)
0 restraints	
Hydrogen site location: mixed	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.29353 (4)	0.65791 (2)	0.59184 (2)	0.01687 (4)
O1	0.56607 (10)	0.47315 (6)	0.32954 (3)	0.01617 (10)
O2	−0.07675 (10)	0.65590 (6)	0.16589 (4)	0.01625 (10)
O3	0.24892 (10)	0.71309 (4)	0.08834 (3)	0.01128 (8)
N1	0.29316 (11)	0.32887 (5)	0.42498 (3)	0.00925 (8)
H11N	0.230 (3)	0.2667 (12)	0.4002 (8)	0.014*
H12N	0.280 (3)	0.3155 (11)	0.4782 (8)	0.014*
H13N	0.461 (3)	0.3287 (11)	0.4122 (7)	0.014*
N2	0.21065 (12)	0.55612 (5)	0.27617 (3)	0.01213 (9)
H2N	0.044 (3)	0.5631 (11)	0.2749 (8)	0.015*
C1	0.37117 (14)	0.56727 (6)	0.50511 (4)	0.01293 (10)
H1D	0.471236	0.613218	0.465519	0.016*
H1E	0.475036	0.499402	0.522492	0.016*
C2	0.12412 (13)	0.52445 (6)	0.46605 (4)	0.01108 (9)
H2A	0.028903	0.593014	0.445308	0.013*
H2B	0.017812	0.486494	0.507971	0.013*
C3	0.16563 (12)	0.43738 (5)	0.39633 (3)	0.00966 (9)
H3	−0.003367	0.416245	0.372606	0.012*
C4	0.33345 (12)	0.48982 (6)	0.32997 (4)	0.01035 (9)
C5	0.34421 (13)	0.61524 (6)	0.21120 (4)	0.01259 (10)
H5A	0.459462	0.559260	0.183793	0.015*
H5B	0.448980	0.679543	0.233724	0.015*
C6	0.15608 (12)	0.66476 (6)	0.15042 (3)	0.00962 (9)
C7	0.59992 (18)	0.66260 (8)	0.64043 (6)	0.02365 (16)
H7A	0.662481	0.582565	0.648561	0.035*
H7B	0.584132	0.701884	0.692882	0.035*
H7C	0.719997	0.705915	0.606324	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01555 (8)	0.01596 (7)	0.01911 (8)	0.00057 (6)	0.00040 (6)	−0.00632 (6)
O1	0.00866 (19)	0.0242 (2)	0.0157 (2)	0.00274 (18)	0.00070 (17)	0.00795 (19)
O2	0.00915 (19)	0.0230 (2)	0.0166 (2)	−0.00048 (18)	0.00041 (16)	0.01047 (19)
O3	0.0129 (2)	0.01408 (18)	0.00689 (15)	−0.00366 (14)	0.00063 (14)	0.00177 (14)
N1	0.00953 (18)	0.01015 (17)	0.00807 (17)	0.00097 (16)	−0.00063 (15)	0.00075 (14)
N2	0.0095 (2)	0.0172 (2)	0.00969 (19)	0.00194 (19)	0.00069 (17)	0.00605 (17)
C1	0.0123 (2)	0.0118 (2)	0.0147 (2)	−0.0001 (2)	0.0012 (2)	−0.00119 (19)
C2	0.0104 (2)	0.0112 (2)	0.0117 (2)	0.00167 (18)	0.00146 (18)	0.00075 (18)

C3	0.0085 (2)	0.0115 (2)	0.0090 (2)	0.00079 (17)	−0.00053 (16)	0.00217 (16)
C4	0.0096 (2)	0.0131 (2)	0.00842 (19)	0.00101 (18)	−0.00038 (17)	0.00254 (17)
C5	0.0094 (2)	0.0181 (3)	0.0103 (2)	0.0009 (2)	0.00068 (18)	0.00519 (19)
C6	0.0102 (2)	0.0109 (2)	0.00774 (19)	−0.00110 (18)	−0.00008 (16)	0.00155 (17)
C7	0.0228 (4)	0.0199 (3)	0.0283 (4)	−0.0025 (3)	−0.0075 (3)	−0.0061 (3)

Geometric parameters (Å, º)

S1—C7	1.7995 (9)	C1—H1D	0.9900
S1—C1	1.8150 (7)	C1—H1E	0.9900
O1—C4	1.2365 (8)	C2—C3	1.5379 (9)
O2—C6	1.2534 (9)	C2—H2A	0.9900
O3—C6	1.2635 (8)	C2—H2B	0.9900
N1—C3	1.4855 (8)	C3—C4	1.5297 (9)
N1—H11N	0.885 (14)	C3—H3	1.0000
N1—H12N	0.896 (13)	C5—C6	1.5186 (9)
N1—H13N	0.907 (14)	C5—H5A	0.9900
N2—C4	1.3342 (8)	C5—H5B	0.9900
N2—C5	1.4499 (9)	C7—H7A	0.9800
N2—H2N	0.879 (15)	C7—H7B	0.9800
C1—C2	1.5296 (10)	C7—H7C	0.9800

C7—S1—C1	99.74 (4)	N1—C3—C2	111.31 (5)
C3—N1—H11N	110.5 (9)	C4—C3—C2	111.53 (5)
C3—N1—H12N	114.9 (8)	N1—C3—H3	108.9
H11N—N1—H12N	106.8 (12)	C4—C3—H3	108.9
C3—N1—H13N	111.5 (8)	C2—C3—H3	108.9
H11N—N1—H13N	105.0 (12)	O1—C4—N2	124.13 (6)
H12N—N1—H13N	107.6 (12)	O1—C4—C3	120.88 (6)
C4—N2—C5	121.62 (6)	N2—C4—C3	114.95 (6)
C4—N2—H2N	123.3 (8)	N2—C5—C6	110.43 (6)
C5—N2—H2N	115.0 (8)	N2—C5—H5A	109.6
C2—C1—S1	108.98 (5)	C6—C5—H5A	109.6
C2—C1—H1D	109.9	N2—C5—H5B	109.6
S1—C1—H1D	109.9	C6—C5—H5B	109.6
C2—C1—H1E	109.9	H5A—C5—H5B	108.1
S1—C1—H1E	109.9	O2—C6—O3	125.28 (6)
H1D—C1—H1E	108.3	O2—C6—C5	118.01 (5)
C1—C2—C3	113.76 (6)	O3—C6—C5	116.70 (6)
C1—C2—H2A	108.8	S1—C7—H7A	109.5
C3—C2—H2A	108.8	S1—C7—H7B	109.5
C1—C2—H2B	108.8	H7A—C7—H7B	109.5
C3—C2—H2B	108.8	S1—C7—H7C	109.5
H2A—C2—H2B	107.7	H7A—C7—H7C	109.5
N1—C3—C4	107.17 (5)	H7B—C7—H7C	109.5

C7—S1—C1—C2	165.35 (5)	C2—C3—C4—O1	93.98 (8)
S1—C1—C2—C3	−174.71 (4)	N1—C3—C4—N2	154.05 (6)

C1—C2—C3—N1	62.23 (7)	C2—C3—C4—N2	−83.89 (7)
C1—C2—C3—C4	−57.41 (7)	C4—N2—C5—C6	169.26 (6)
C5—N2—C4—O1	0.09 (11)	N2—C5—C6—O2	4.52 (9)
C5—N2—C4—C3	177.89 (6)	N2—C5—C6—O3	−176.26 (6)
N1—C3—C4—O1	−28.08 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11*N*···O2^{i}	0.885 (14)	1.854 (14)	2.7290 (8)	169.5 (13)
N1—H11*N*···O3^{i}	0.885 (14)	2.593 (15)	3.1465 (8)	121.4 (11)
N1—H12*N*···O3^{ii}	0.896 (13)	1.857 (13)	2.7531 (7)	179.6 (14)
N1—H13*N*···O3^{iii}	0.907 (14)	2.015 (14)	2.7529 (8)	137.5 (11)
N1—H13*N*···O1	0.907 (14)	2.211 (13)	2.6940 (8)	112.7 (10)
N2—H2*N*···O2	0.879 (15)	2.185 (13)	2.6273 (8)	110.6 (10)

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