

trans-*S,S'*-(But-2-ene-1,4-diyl)bis(L-cysteine) dihydrate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.041

wR factor = 0.089

Data-to-parameter ratio = 11.9

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2 \cdot 2\text{H}_2\text{O}$, the two cysteine moieties (zwitterions), separated by the rigid butene-1,4-diyl chain, adopt different conformations. These are characterized by the fact that the first S atom is *anti* to the carboxyl group in one moiety while the second S atom is *gauche* to both the carboxyl and protonated amino groups in the other moiety. The cysteine moieties and water molecules are linked by hydrogen bonds, forming a 14-membered ring within the *ac* plane and layer connections along the *b* axis, which bind the structure together in three dimensions.

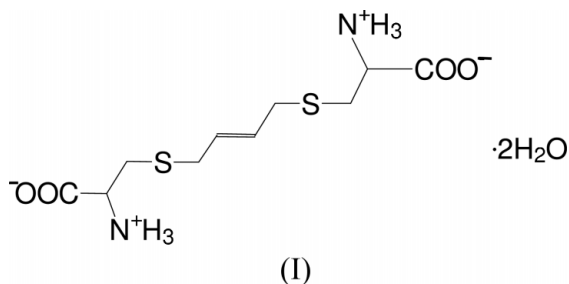
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Comment

L-Cysteine is one of the essential amino acids in nature. Some of its derivatives present remarkable bioactivity, and they can be used as antioxidants, antibacterial agents (Rabinkov *et al.*, 1998) and chemical precursors of antitumor medicines (Hakimelahi *et al.*, 2002). Although the crystal structure of both L-cysteine (Kerr & Ashmore, 1973, 1975; Görbitz & Dalhus, 1996; Harding & Long, 1968) and DL-cysteine (Luger & Weber, 1999) have been reported, structures of bis(L-cysteine) derivatives are rare in the literature (Bigoli *et al.*, 1982).



In this paper, the structure of the title compound, *trans*-*S,S'*-(but-2-ene-1,4-diyl)bis(L-cysteine) dihydrate, (I), is reported. The molecular structure of (I) is illustrated in Fig. 1.

The molecule of (I) has a *trans* configuration. The distance between atoms C5 and C6 is 1.299 (5) Å, which is shorter than the distance of 1.34 (1) Å for a normal C=C bond (Lide, 1992–1993) and the distance of 1.326 Å in *trans*-2,5-dimethyl-3-hexene-2,5-diol. The angles C4–C5–C6 and C5–C6–C7 are 125.6 (3) and 123.5 (3)°, respectively, which are slightly smaller than those of 127.4 and 124.9° in *trans*-2,5-dimethyl-3-hexene-2,5-diol (Ruysink & Vos, 1974). The torsion angle C4–C5–C6–C7 is 177.7 (4)°, indicating that the butenediyl group is almost planar. The C–S bond lengths [C3–S2 = 1.794 (4), C4–S2 = 1.812 (4), C7–S1 = 1.820 (4) and C8–S1 =

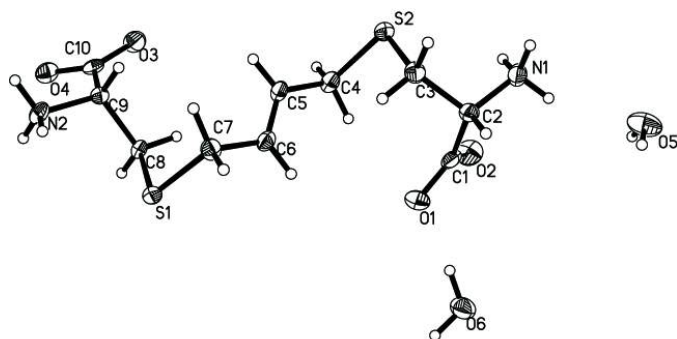


Figure 1
View of the molecular structure of (I), with 30% probability ellipsoids, H atoms are shown as small spheres of arbitrary radii.

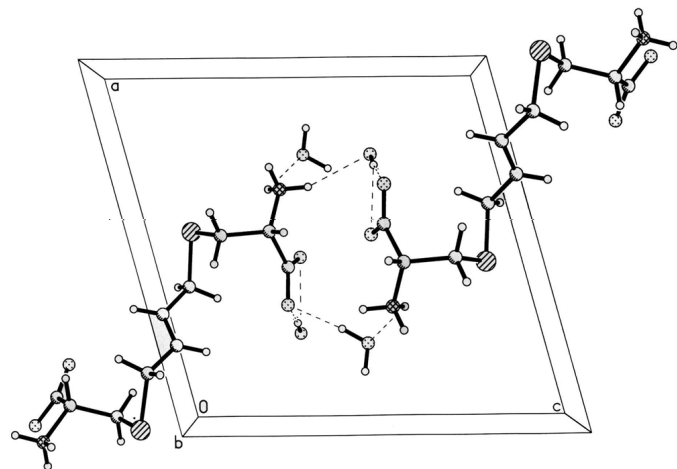


Figure 2
The unit-cell contents of (I), showing a 14-membered hydrogen bond.

1.80 (4) Å] are of the same magnitude as the value of 1.811 (3) Å in L-cysteine (Kerr & Ashmore, 1973). The bond angles C3–S2–C4 and C8–S1–C7 are 102.1 (2) and 100.4 (2)°, respectively, slightly larger than the value of 99.05° in dimethyl sulfide (Lide, 1992–1993).

The difference in the C–O bond lengths of the two carboxyl groups is obviously influenced by the hydrogen-bond environment (Table 2). Atoms O1 and O4 are involved in more than one hydrogen bond (O6–H3···O1, O5–H2···O1 and O5–H1···O1; N2–H2b···O4 and O6–H4···O4), while atoms O2 and O3 only take part in one hydrogen-bond interaction, which may explain why the C1–O1 [1.252 (5) Å] and C10–O4 [1.263 (4) Å] bond lengths are longer than those of C1–O2 [1.218 (6) Å] and C10–O3 [1.231 (5) Å].

The two cysteine moieties (zwitterions), separated by the rigid butene-1,4-diyl skeleton, adopt different conformations. Atom S1 is *anti* to the C10/O3/O4 carboxyl group, with a S1–C8–C9–C10 torsion angle of 178.4°. However, atom S2 is *gauche* with respect to both the C1/O1/O2 carboxyl and protonated amino groups; the corresponding torsion angles, S2–C3–C2–C1 and S2–C3–C2–N1, are 61.8 (4) and 57.8 (4)°, respectively. The difference is clearly illustrated by the Newman projection shown in Fig. 4.

The molecules are arranged in the crystal lattice parallel to the *ac* plane, in which two N–H groups of the protonated

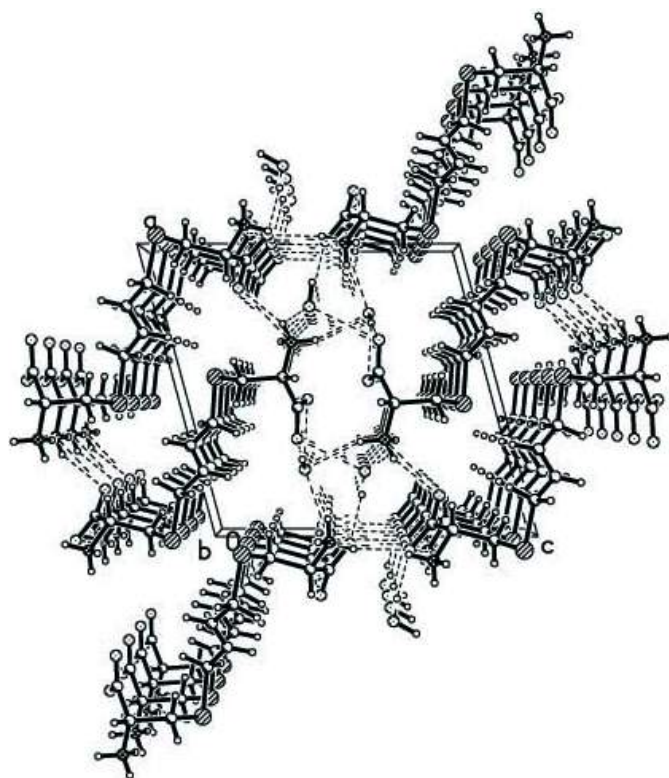


Figure 3
A packing diagram of (I), viewed along the *b* axis.

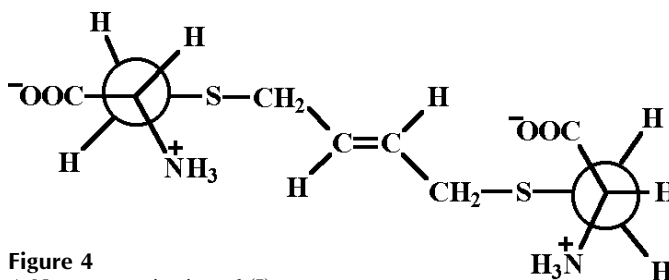


Figure 4
A Newman projection of (I).

amino group and two C–O groups of the carboxyl group, as well as two water molecules, form a 14-membered ring *via* hydrogen bonds. Interestingly, these molecules are linked together through hydrogen bonds along the *b* axis to form a three-dimensional network with an infinite tunnel.

Besides overwhelming intermolecular hydrogen bonding, there exists one intramolecular hydrogen-bond interaction (N2–H2b···O4) in the S1/C8/C9/C10/N2 moiety. No such interaction is found in the other moiety, which may explain the conformational differences of the two zwitterion moieties.

Experimental

Compound (I) was synthesized by a modified literature method (Kalopissis & Manousses, 1975). A solution of 5.35 g (0.0025 mol) of *trans*-1,4-dibromo-2-butene in 5 ml ethanol was added dropwise to a mixture of 0.88 g (0.005 mol) of L-cysteine hydrochloride monohydrate, 1 ml of 10 mol l⁻¹ sodium hydroxide, 5 ml of water and 7.5 ml of ethanol. The reaction mixture was then stirred for 10 h at room temperature. The precipitate was filtered off and recrystallized

from water. Needle-like colorless crystal were obtained (yield 68%; m.p. 513–515 K (decomposition)); IR (KBr): 3479 (*b*), 3024 (*b*), 2924 (*s*), 1687 (*w*), 1613 (*vs*, *b*), 1483 (*s*), 1419 (*s*), 1393 (*s*), 1342 (*s*), 1303 (*s*), 1069 (*w*), 1045 (*w*), 966 (*vs*) cm^{-1} ; $^1\text{H NMR}$ (D_2O): δ 5.65 (2H, *bs*), 4.17 (2H, *t*), 3.23 (4H, *bs*), 3.14 (2H, *d*), 3.00 (2H, *dd*) p.p.m. 10 mg of (I) was dissolved in 10 ml hot distilled water and, after filtration, the solution was kept at room temperature for 10 d yielding colorless single crystals of (I), suitable for X-ray analysis.

Crystal data

$\text{C}_{10}\text{H}_{22}\text{N}_2\text{O}_6\text{S}_2$	$D_x = 1.453 \text{ Mg m}^{-3}$
$M_r = 330.42$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1870 reflections
$a = 11.672$ (4) Å	$\theta = 2.7\text{--}23.1^\circ$
$b = 5.3982$ (19) Å	$\mu = 0.38 \text{ mm}^{-1}$
$c = 12.413$ (4) Å	$T = 293$ (2) K
$\beta = 105.020$ (5)°	Prism, colorless
$V = 755.4$ (4) Å ³	$0.30 \times 0.15 \times 0.10 \text{ mm}$
$Z = 2$	

Data collection

Bruker CCD area-detector diffractometer	2338 independent reflections
φ and ω scans	1894 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.895$, $T_{\text{max}} = 0.963$	$\theta_{\text{max}} = 25.0^\circ$
3157 measured reflections	$h = -13 \rightarrow 8$
	$k = -5 \rightarrow 6$
	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} = 0.026$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
2338 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
197 parameters	Absolute structure: (Flack, 1983),
H atoms treated by a mixture of independent and constrained refinement	847 Friedel pairs
	Flack parameter = 0.06 (10)

Table 1

Selected geometric parameters (Å, °).

N1—C2	1.487 (5)	C4—C5	1.491 (5)
N2—C9	1.483 (5)	C6—C7	1.494 (5)
C1—C2	1.536 (6)	C8—C9	1.522 (4)
C2—C3	1.514 (5)	C9—C10	1.514 (6)
O2—C1—O1	125.8 (4)	C5—C6—C7	123.5 (3)
O2—C1—C2	118.4 (4)	C9—C8—S1	115.3 (3)
O1—C1—C2	115.7 (5)	N2—C9—C10	110.6 (3)
N1—C2—C3	110.1 (3)	N2—C9—C8	109.9 (3)
N1—C2—C1	107.4 (4)	C10—C9—C8	109.4 (3)
C3—C2—C1	112.1 (3)	O3—C10—O4	125.2 (4)
C2—C3—S2	115.8 (3)	O3—C10—C9	117.4 (3)
C6—C5—C4	125.6 (3)	O4—C10—C9	117.3 (4)
O2—C1—C2—N1	−11.6 (5)	C7—S1—C8—C9	−77.6 (3)
O1—C1—C2—N1	170.3 (3)	S1—C8—C9—N2	−56.9 (3)
O2—C1—C2—C3	109.5 (4)	N2—C9—C10—O3	165.9 (3)
O1—C1—C2—C3	−68.6 (5)	C8—C9—C10—O3	−72.9 (4)
C5—C6—C7—S1	108.5 (4)	N2—C9—C10—O4	−16.4 (4)
C8—S1—C7—C6	−61.1 (3)	C8—C9—C10—O4	104.9 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1C···O5	0.89	2.22	3.053 (5)	157
O6—H3···O1	0.93 (4)	1.90 (3)	2.787 (4)	159 (6)
N2—H2D···O5 ⁱ	0.89	1.97	2.788 (5)	152
N2—H2B···O4 ⁱⁱ	0.89	1.99	2.864 (4)	165
O6—H4···O4 ⁱⁱⁱ	0.92 (3)	1.89 (3)	2.805 (4)	174 (4)
O5—H2···O2 ^{iv}	0.93 (3)	2.03 (3)	2.821 (5)	142 (4)
O5—H2···O1 ^{iv}	0.93 (3)	2.26 (2)	3.122 (5)	156 (4)
O5—H1···O1 ^v	0.92 (3)	1.80 (2)	2.709 (5)	175 (5)

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

The water H atoms were located in a difference Fourier map and refined using constraints. All other H atoms were located in difference Fourier maps, positioned geometrically and refined as riding on their parent atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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