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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.016 \text{ \AA}$
R factor = 0.045
wR factor = 0.087
Data-to-parameter ratio = 7.2

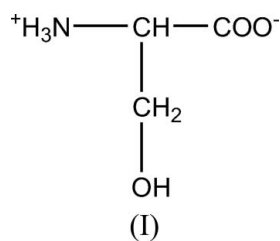
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

L-Serine III at 8.0 GPa

The structure of a new high-pressure polymorph of L-serine (form III), $\text{C}_3\text{H}_7\text{NO}_3$, was solved and refined at 8 GPa by single-crystal X-ray diffraction in a diamond anvil cell *in situ*. The existence of this form was supposed from Raman spectroscopy [Kolesnik *et al.* (2005). *Dokl. Phys. Chem.* **404**, 61–64 (in Russian), 169–172 (in English)], but its structure remained unknown. Form III preserves the space group $P2_12_12_1$ of the two other forms of L-serine; the conformation of the zwitterion and the intermolecular hydrogen bonding in form III differ from those in forms I and II.

Comment

Two pressure-induced polymorphic transitions were reported for L-serine giving form II at 5.3 GPa and form III at 7.8 GPa (Kolesnik *et al.*, 2005; Moggach *et al.*, 2005). The structure of form II was solved from single-crystal X-ray diffraction data *in situ* (Moggach *et al.*, 2005). For form III, the Raman spectrum was measured (Kolesnik *et al.*, 2005), but the crystal structure remained unknown.



In the present work the existence of the high-pressure form III of L-serine, (I), was clearly confirmed. During a phase transition II to III, unit-cell parameter *a* increased from 5.5578 (5) Å at 7.5 GPa to 5.6117 (9) Å at 8.0 GPa; parameters *b* and *c* decreased slightly, and as a result only a slight kink could be noticed in the $V(P)$ dependence. Compared with forms I (Kistenmacher *et al.*, 1974) and II, the main structural pattern (head-to-tail chains of zwitterions along axis *a* linked with each other along *b* and *c* in a three-dimensional hydrogen-bonded network) is preserved to a large extent.

The conformation of the zwitterions in L-serine III (Table 1 and Fig. 1) differs from that in L-serine forms I and II, respectively. The largest changes involve the dihedral angles between the planes N1/C2/C3 and C2/C3/O3 [60 (1), 44 (2) and 54 (1)° in forms I at 4.2 GPa, II at 7.5 GPa and III, respectively] and O1/C1/O2 and N1/C2/C3 [60 (2), 62 (2) and 47 (2)° in forms I at 4.2 GPa, II at 7.5 GPa and III, respectively]. Interestingly, during the II to III transition, the dihedral angle between the planes O1/C1/O2 and C1/C2/C3

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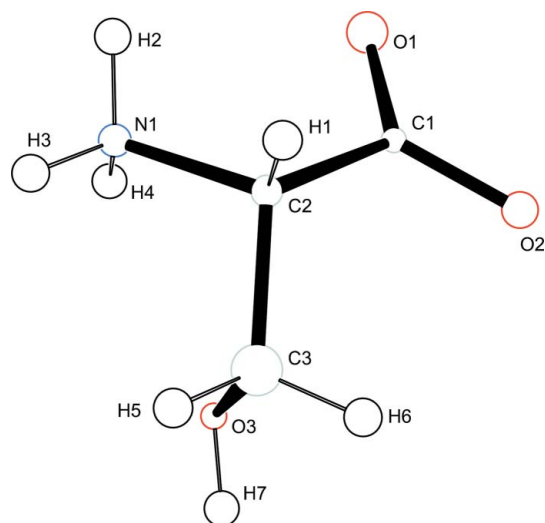


Figure 1
A view of the molecular structure of L-serine III with the atom-labeling scheme. Displacement spheres are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

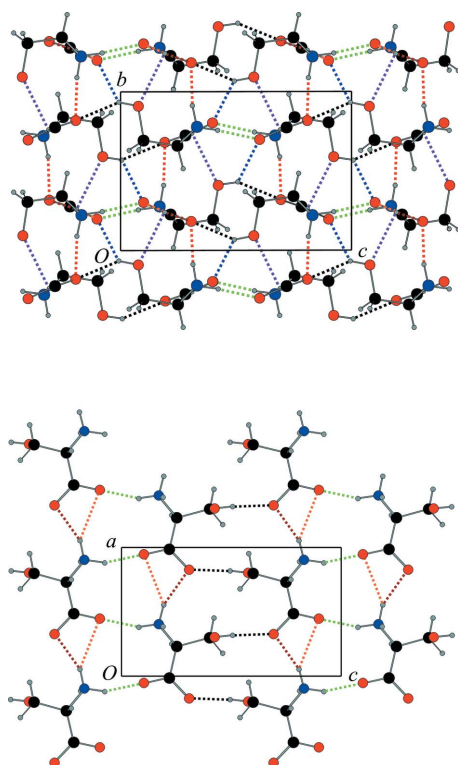


Figure 2
Fragments of the crystal packing of L-serine III viewed along the axes *a* (top) and *b* (bottom). The dashed lines denote the hydrogen bonds.

remains almost unchanged, in contrast to the case of the I to II transition [60 (1), 41 (2) and 39 (1)° in forms I at 4.2 GPa, II at 7.5 GPa and III, respectively].

The aforementioned conformational changes in zwitterions in L-serine III are mainly caused by the reorganization of the hydrogen-bonded network (Table 2) in the crystal structure

under increasing pressure. During the II to III phase transition, the existing OH...O(CO) hydrogen bonds are preserved and shorten slightly. At the same time, an additional longer OH...O(CO) hydrogen bond appears, as well as a new NH...OH hydrogen bond (Table 2 and Fig. 2), so the OH group in L-serine form III is not only a proton donor, as in form II (Moggach *et al.*, 2005), but also a proton acceptor, as it was in form I (Kistenmacher *et al.*, 1974).

Experimental

L-Serine was purchased from ICN Biomedicals (102873 RT). Single crystals were selected from the purchased sample. In order to reach higher pressures, smaller blocks were cut, the prisms being elongated along crystallographic direction [100]. Hydrostatic pressure 8 GPa was created in the DAC without Be supports (Ahsbahs, 2004). Gasket material: Thyrodur-2709, starting thickness 0.180 mm, preindented to 0.100 mm and then hardened by heating/cooling (Ahsbahs, 1996), hole diameter 0.300 mm. Absolute methanol to ethanol of 4:1 volume ratio was used as pressure-transmitting liquid (Fujishiro *et al.*, 1981).

Crystal data

$C_3H_7NO_3$	$Z = 4$
$M_r = 105.10$	$D_x = 1.991 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 5.6117 (9) \text{ \AA}$	$\mu = 0.18 \text{ mm}^{-1}$
$b = 6.556 (2) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 9.5321 (12) \text{ \AA}$	Block, colorless
$V = 350.69 (13) \text{ \AA}^3$	$0.16 \times 0.08 \times 0.05 \text{ mm}$

Data collection

Stoe four-circle diffractometer	53 reflections with $I > 2\sigma(I)$
Fixed φ mode, ω scans	$R_{\text{int}} = 0.071$
Absorption correction: none	$\theta_{\text{max}} = 20.0^\circ$
426 measured reflections	2 standard reflections
217 independent reflections	every 20 reflections
	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2)]$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.39$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
217 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
30 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—O1	1.244 (12)	C2—N1	1.469 (16)
C1—O2	1.254 (11)	C2—C3	1.476 (13)
C1—C2	1.492 (16)	C3—O3	1.430 (19)
O1—C1—O2	125.4 (11)	N1—C2—C1	110.2 (11)
O1—C1—C2	118.0 (10)	C3—C2—C1	113.2 (10)
O2—C1—C2	116.4 (9)	O3—C3—C2	107.2 (11)
N1—C2—C3	106.1 (11)		
O1—C1—C2—N1	25 (2)	O2—C1—C2—C3	−41 (2)
O2—C1—C2—N1	−159.9 (13)	N1—C2—C3—O3	53.8 (14)
O1—C1—C2—C3	143.7 (15)	C1—C2—C3—O3	−67.2 (14)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H3 \cdots O2 ⁱ	0.89	1.93	2.782 (11)	159
N1–H3 \cdots O1 ⁱ	0.89	2.41	3.117 (11)	136
N1–H4 \cdots O2 ⁱⁱ	0.89	2.16	2.966 (19)	151
N1–H2 \cdots O1 ⁱⁱⁱ	0.89	1.79	2.639 (12)	159
O3–H7 \cdots O2 ^{iv}	0.82	1.93	2.651 (13)	146
O3–H7 \cdots O1 ^v	0.82	2.36	2.898 (15)	124
N1–H3 \cdots O3 ^{vi}	0.89	2.55	3.04 (2)	115

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

Cell parameters were refined using a special procedure described by King & Finger (1979), based on measuring each reflection in eight positions. Data collection was carried out in a fixed φ mode (Finger & King, 1978). Data reduction was performed with an original program analyzing the reflection profiles and comparing equivalents. Because of the small size of the crystal and the restrictions imposed at measuring reflections in a diamond anvil cell, *ab initio* data solution was not possible. The structure of L-serine II at 5.4 GPa (Moggach *et al.*, 2005) was taken as the starting model and then refined isotropically. All H atoms were placed at idealized positions and then treated as riding atoms with C–H = 0.97 and 0.98 Å, N–H = 0.89 Å, and O–H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ or $1.5U_{\text{iso}}(\text{N}, \text{O})$. In the absence of significant anomalous scattering effects, Friedel pairs have been merged.

Data collection: in house program, fixed φ mode (Finger & King, 1978); cell refinement: in-home program, reflections in eight positions (King & Finger, 1979); data reduction: in-home program, profile

analysis; program(s) used to solve structure: starting model for L-serine II (Moggach *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PowderCell* (Kraus & Nolze, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *SHELXL97*.

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