

L-Alanylglycyl-L-alanine monohydrate  
at 20 K

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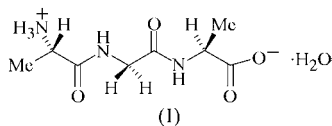
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The X-ray crystal structure of the title compound,  $C_8H_{15}N_3O_4 \cdot H_2O$ , at 20 K (space group  $P2_1$ ) reveals that the molecular conformation of the tripeptide is remarkably different from the water-free form (space group  $P2_12_12_1$ ) reported previously [Padiyar & Seshadri (1996), *Acta Cryst. C* **52**, 1693–1695].

## Comment

In the course of our ongoing charge-density investigations on oligopeptides, we became interested in some comparative studies of tripeptides of the type Ala-*Xxx*-Ala, where *Xxx* was to be varied among the 20 naturally encoded amino acids. An initial charge-density study was performed on the homotripeptide (L-Ala)<sub>3</sub> (Rödel, 2003). In a further step, we considered the system L-alanylglycyl-L-alanine, the conventional X-ray crystal structure of which (with spherical scattering factors) had previously been determined at room temperature (Padiyar & Seshadri, 1996). In a number of recrystallization attempts, we were unable to reproduce the literature modification. However, we were able to grow crystals of the title monohydrate, (I), while the structure reported by Padiyar & Seshadri (1996) is solvent free. We present here the previously unreported structure of L-Ala-Gly-L-Ala- $H_2O$ , (I), based on a low-order X-ray data set ( $d = 0.70 \text{ \AA}$ ) taken at 20 K.



The structure of the asymmetric unit of (I), together with the atomic numbering scheme, is shown in Fig. 1, with the displacement parameters at 20 K. The tripeptide exists in the zwitterionic form in the crystal. Bond lengths and angles are as expected and need no detailed discussion. A tendency of the 20 K structure to have slightly longer bonds than the room-temperature water-free structure (up to 0.027 Å longer) could be expected.

Apart from the space group ( $P2_12_12_1$  for the water-free form and  $P2_1$  for the monohydrate), the two conformational

isomers differ considerably in the torsion angles of the terminal groups (Table 1 and Fig. 2). This holds for  $\psi_1$  at the N terminus and is even more pronounced for  $\varphi_3$ . This angle is  $-159.1 (2)^\circ$  for (I), indicating an almost *trans* arrangement of the carboxylate group with respect to the N3–C4 peptide bond, while it is  $-71.3 (2)^\circ$  for the water-free form, describing a *gauche* conformation in this region. All further conformational torsion angles of the two molecules agree to within 5–15°.

The crystal packing of (I) is illustrated in Fig. 3, with the hydrogen bonds indicated by dashed lines. The hydrogen bonds are also summarized in Table 2. The twofold screw axis generates a head-to-tail arrangement of two molecules in the *ac* plane linked by three hydrogen bonds, *viz.* N1–H11A...O4<sup>i</sup>, N3–H13...O1<sup>i</sup> and O4...H11C<sup>iii</sup>–N1<sup>iii</sup> (symmetry codes as in Table 2). The screw axis also generates a helical linkage of this molecular pair in the *b* direction. Molecules related by a pure translation in the *c* direction are connected by a bifurcated hydrogen bond from the ammonium N1–H11B to both oxygen acceptors of the carboxylic acid group, with the N1–H11B...O4<sup>ii</sup> hydrogen bond being rather weak. A further interaction in the *ac* plane is also seen in the *a* direction, where neighbouring layers are linked *via* the

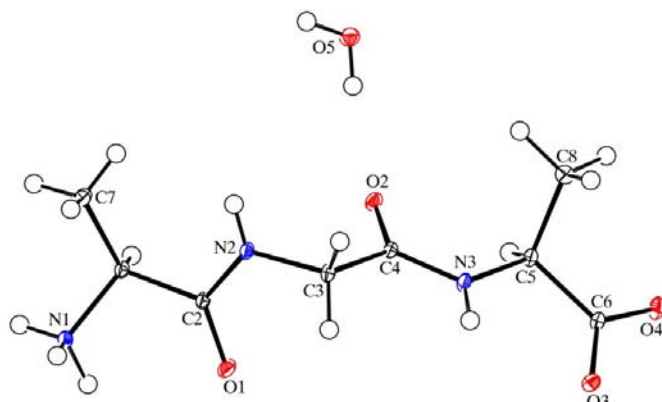


Figure 1

The molecular structure and atom-numbering scheme of (I). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

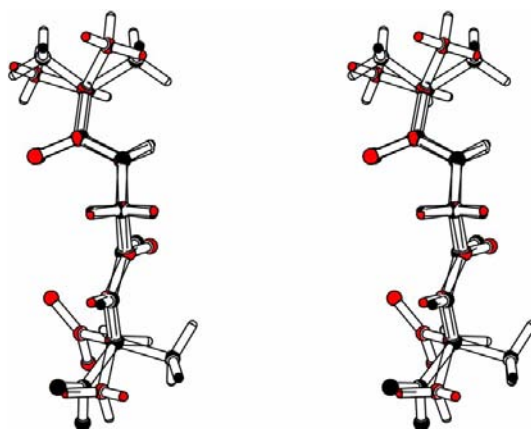
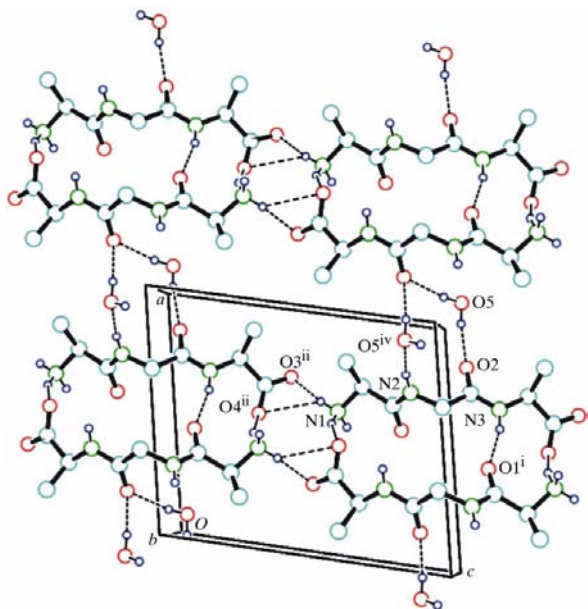


Figure 2

A fit of L-alanylglycyl-L-alanine in the monohydrate (this work) and water-free forms (Padiyar & Seshadri, 1996).



**Figure 3**  
The crystal packing of (I), projected on to the *ac* plane. Hydrogen bonds are indicated by dashed lines and symmetry codes are as in Table 2.

water molecule, establishing a cycle of four (three independent) hydrogen bonds, *viz.* N2—H12...O5<sup>iv</sup>—H25A<sup>iv</sup>...O2<sup>iv</sup>...H25B—O5—H25A...O2—C4—C3—N2 (symmetry code as in Table 2). Except for two weak C—H...O interactions, no further intermolecular contacts of interest exist.

## Experimental

Crystals of (I) were grown by evaporation from an aqueous solution of L-alanyl-glycyl-L-alanine (Bachem, Germany).

### Crystal data

C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> ·H <sub>2</sub> O	$D_x = 1.366 \text{ Mg m}^{-3}$
$M_r = 235.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1009 reflections
$a = 10.207(6) \text{ \AA}$	$\theta = 2.9\text{--}24.7^\circ$
$b = 4.780(3) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 11.955(7) \text{ \AA}$	$T = 20(1) \text{ K}$
$\beta = 101.39(1)^\circ$	Needle, colourless
$V = 571.8(6) \text{ \AA}^3$	$0.4 \times 0.3 \times 0.2 \text{ mm}$
$Z = 2$	

### Data collection

Huber diffractometer with Bruker APEX CCD area detector	$R_{\text{int}} = 0.027$
$\varphi$ scans	$\theta_{\text{max}} = 30.0^\circ$
13 577 measured reflections	$h = -13 \rightarrow 14$
1851 independent reflections	$k = -5 \rightarrow 6$
1811 reflections with $I > 2\sigma(I)$	$l = -16 \rightarrow 16$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.1445P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
1851 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
213 parameters	
All H-atom parameters refined	

**Table 1**

Comparison of selected torsion angles ( $^\circ$ ) for L-alanyl-glycyl-L-alanine monohydrate, (I), and the water-free form, (II) (Padiyar & Seshadri, 1996).

For definitions of nomenclature, see IUPAC–IUB Commission on Biochemical Nomenclature (1970).

Torsion angle	Nomenclature	(I)	(II)
N1—C1—C2—N2	$\psi_1$	−146.8 (2)	172.6 (2)
C1—C2—N2—C3	$\omega_1$	−173.5 (2)	−178.2 (2)
C2—N2—C3—C4	$\varphi_2$	86.4 (2)	91.7 (1)
N2—C3—C4—N3	$\psi_2$	−167.4 (2)	−151.9 (2)
C3—C4—N3—C5	$\omega_2$	−173.8 (2)	−176.9 (1)
C4—N3—C5—C6	$\varphi_3$	−159.1 (2)	−71.3 (2)
N3—C5—C6—O4	$\psi_{3,2}$	−5.0 (3)	−6.9 (1)

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H11A...O4 <sup>i</sup>	0.89 (2)	2.03 (2)	2.859 (2)	154 (2)
N1—H11B...O3 <sup>ii</sup>	0.90 (2)	1.87 (2)	2.763 (2)	169 (2)
N1—H11B...O4 <sup>ii</sup>	0.90 (2)	2.59 (2)	3.272 (2)	133 (2)
N1—H11C...O4 <sup>iii</sup>	0.93 (2)	1.88 (2)	2.760 (2)	156 (2)
N2—H12...O5 <sup>iv</sup>	0.84 (2)	2.02 (2)	2.815 (2)	157 (2)
N3—H13...O1 <sup>i</sup>	0.88 (2)	2.04 (2)	2.885 (2)	163 (2)
O5—H25A...O2	0.85 (2)	1.92 (2)	2.750 (2)	165 (2)
O5—H25B...O2 <sup>iv</sup>	0.86 (2)	1.94 (2)	2.798 (2)	171 (2)

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

All H atoms were found in difference Fourier maps and refined freely.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINTE* (Siemens, 1996) and *SADABS* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *SCHAKAL99* (Keller & Pierrard, 1999); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1135). Services for accessing these data are described at the back of the journal.

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