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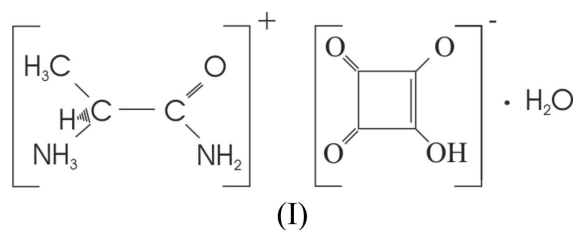
Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.049
 wR factor = 0.134
Data-to-parameter ratio = 10.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.1-(Aminocarbonyl)ethylammonium
hydrogensquarate monohydrate

Cations of the title compound, $\text{C}_3\text{H}_9\text{N}_2\text{O}^+ \cdot \text{C}_4\text{HO}_4^- \cdot \text{H}_2\text{O}$, are connected by intermolecular $\text{N}_{\text{ammonium}}-\text{H} \cdots \text{O}_{\text{amide}}$ hydrogen bonds into helical chains propagating in the [010] direction. These chains are further linked by $\text{N}_{\text{ammonium}}-\text{H} \cdots \text{O}$ hydrogen bonds to the hydrogensquarate anions, which in turn form $\text{O}-\text{H} \cdots \text{O}$ -bridged chains in the [100] direction, thereby giving rise to a three-dimensional network. The water O atoms participate in two $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to the anions and one $\text{O} \cdots \text{H}-\text{N}_{\text{amide}}$ bridge to the cation.

Comment

In the course of our spectroscopic and structural studies of some optically active derivatives of amino acids, having nonlinear optical and electro-optical properties (Nalwa *et al.* 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987), the crystal structure of the title compound, L-alaninium amide hydrogensquarate monohydrate, (I), has been determined. C-amidated amino acids and their salts and ester amides of squaric acid represent a new class of compounds, having great biological importance. A structural study on the C-amidated amino acids Ile, Val, Thr, Ser, Met, Trp, Gln and Arg has been performed and the results compared with those for the free amino acids (In *et al.* 2001).



The asymmetric unit of (I) is shown in Fig. 1 and a projection of the crystal structure in Fig. 2. Zigzag helical chains are formed by L-alaninium amide cations in the [010] direction by means of hydrogen bonds involving the ammonium groups and the O atoms of the amide groups [$\text{N}2-\text{H}23 \cdots \text{O}1 = 2.819(4)$ Å and $\text{H}23 \cdots \text{O}1 = 1.98$ Å]. Individual components of (I) are connected by intermolecular hydrogen bonds between the amide (N1 and O1), ammonium (N2), water (OW), and hydrogensquarate carbonyl (O1', O2' and O4') and hydroxy (O3') functions (Fig. 2 and Table 1) into an infinite three-dimensional network. Neighbouring hydrogensquarate anions are themselves linked by 1,3 $\text{O}3'-\text{H}3' \cdots \text{O}1'$ hydrogen bonds [$\text{O}3'-\text{H}3' \cdots \text{O}1' = 2.587(3)$ Å and $\text{H}3' \cdots \text{O}1' = 1.77$ Å] and form chains propagating in the [100] direction. 3,4-Hydrogen bonds as part of infinite chains (Angelova, Petrova *et al.*, 1996) and of dimers of hydro-

Received 13 October 2005
Accepted 18 November 2005
Online 26 November 2005

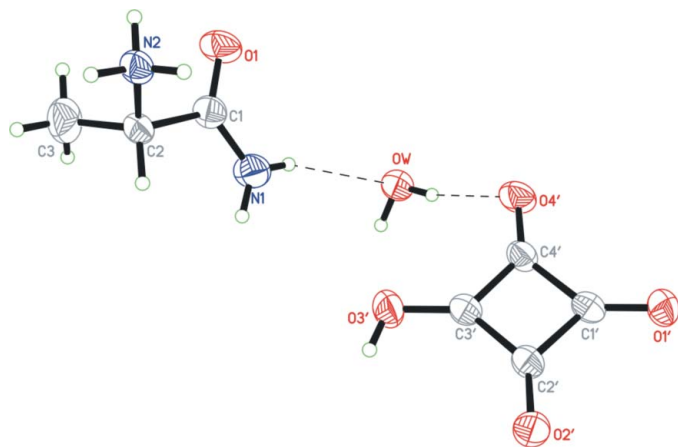


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

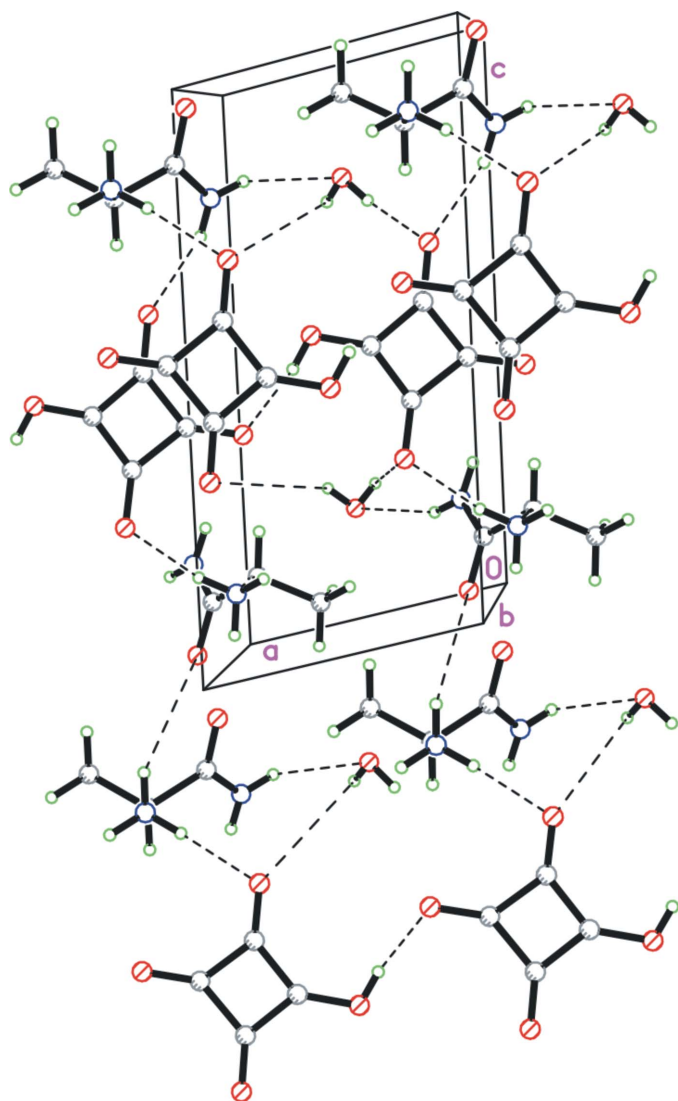


Figure 2
Linkage of the molecules of (I) into a three-dimensional network through intermolecular hydrogen bonds (dashed lines).

gensquarate anions are also known (Angelova, Velikova *et al.*, 1996; Kolev *et al.*, 2004).

Experimental

The starting compound L-alaninium amide acetate is a white powder and was received from Bachem (Switzerland) and recrystallized from water–ethanol (1:1 *v/v*). Compound (I) was isolated by adding a methanol solution (10 ml) of L-alaninium amide acetate (148 mg) to an aqueous solution (14 ml) of squaric acid (114 mg) and leaving the mixture to stand. Colourless prismatic crystals, suitable for X-ray analysis, formed after two weeks and were filtered off and dried under air at room temperature. IR (KBr pellet), cm^{-1} : 3546(*m*), 3397(*s*) $\nu(\text{OH})$, 3290, 3200, 3110 $\nu(\text{NH}_2)$, 3100, 3053, 3036 $\nu(\text{NH}_3)$, 1815(*w*) $\nu(\text{C}-\text{O} + \text{C}=\text{O})$, 1673(*vs*) $\nu(\text{C}=\text{O})$ (amide I), 1630, 1609 $\nu(\text{NH}_3)$, 1604 (amide II), 1491 $\delta(\text{NH}_3)$, 1490, 1349, 1209 $\delta(\text{CH}_3)$, 1382 $\nu(\text{CN})$ (amide III), 1170, 1112, 934 $\rho(\text{NH}_3)$ (rocks), 1129 $\rho(\text{NH}_2)$ (rocks), 789 (amide VII), 711 $\omega(\text{NH}_2) + \delta(\text{C}=\text{O})$ (amide V). Further details of the IR assignment and the Raman bands are given as supplementary material in the CIF file.

Crystal data

$\text{C}_3\text{H}_9\text{N}_2\text{O}^+ \cdot \text{C}_4\text{HO}_4^- \cdot \text{H}_2\text{O}$

$M_r = 220.19$

Monoclinic, $P2_1$

$a = 6.2189$ (12) Å

$b = 6.4643$ (13) Å

$c = 12.790$ (3) Å

$\beta = 101.80$ (3)°

$V = 503.31$ (17) Å³

$Z = 2$

$D_x = 1.453$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 20

reflections

$\theta = 7.9\text{--}16.8^\circ$

$\mu = 0.13$ mm⁻¹

$T = 294$ (2) K

Prism, colourless

$0.44 \times 0.34 \times 0.24$ mm

Data collection

Siemens P4 four-circle

diffractometer

ω scans

Absorption correction: ψ scan

(*SHELXL*; Sheldrick, 1995)

$T_{\text{min}} = 0.941$, $T_{\text{max}} = 0.975$

1708 measured reflections

1580 independent reflections

1260 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\text{max}} = 30.0^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 9$

$l = -17 \rightarrow 17$

3 standard reflections

every 100 reflections

intensity decay: 0.5%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.134$

$S = 1.08$

1580 reflections

145 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.2429P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.36$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Extinction correction: *SHELXL97*

Extinction coefficient: 0.21 (2)

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{N1---H11}\cdots\text{OW}$	0.86	2.32	3.134 (4)	157
$\text{N1---H12}\cdots\text{O4}^{\text{iv}}$	0.86	2.06	2.890 (3)	162
$\text{N2---H21}\cdots\text{O2}^{\text{iii}}$	0.89	1.92	2.777 (3)	160
$\text{N2---H22}\cdots\text{OW}^{\text{iii}}$	0.89	1.96	2.843 (4)	175
$\text{N2---H23}\cdots\text{O1}^{\text{iv}}$	0.89	1.98	2.819 (4)	156
$\text{O3}'\text{---H3}'\cdots\text{O1}^{\text{vi}}$	0.82	1.77	2.587 (3)	171
$\text{OW---HW1}\cdots\text{O4}'$	0.83 (1)	1.98 (2)	2.793 (4)	169 (5)
$\text{OW---HW2}\cdots\text{O2}'^{\text{v}}$	0.83 (1)	1.93 (2)	2.743 (4)	167 (4)

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

In the absence of significant anomalous dispersion effects, Friedel pairs were merged. The *S* configuration of the L-alanine amide C2 atom is known for the natural amino acid and was assigned as such. The water H atoms were located in difference syntheses and refined freely with isotropic displacement factors $U_{\text{iso}}(\text{H}) = 1.35U_{\text{iso}}(\text{OW})$ under the restraint $\text{OW}-\text{H} = 0.83(1) \text{ \AA}$. The H atoms of the cation and anion were constrained to idealized positions and refined using a riding model, with C—H distances of 0.96 Å for the methyl group and 0.98 Å for the α -carbon atom C2, N—H distances of 0.86 Å for the amide H and 0.89 Å for the ammonium H atoms, and a $\text{O}3'-\text{H}3'$ distance of 0.82 Å for the hydrogensquarate hydroxy group. Isotropic displacement factors $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{N}1)$, $U_{\text{iso}}(\text{H}) = 1.30U_{\text{iso}}(\text{N}2, \text{O}3')$ and $U_{\text{iso}}(\text{H}) = 1.35U_{\text{iso}}(\text{C}3, \text{O}W)$ were employed for the respective H atoms.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

TK and MS thank the DAAD for a grant within the priority programme 'Stability Pact South Eastern Europe', the Alex-

ander von Humboldt Foundation and the Bulgarian National Fund for Research (grant No. X-1213).

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