Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

L-Prolinamidium hydrogensquarate

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.031
wR factor = 0.083
Data-to-parameter ratio = 6.5

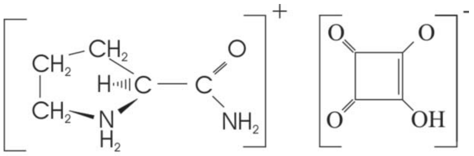
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 20 December 2005
Accepted 22 December 2005
Online 7 January 2006

Cations of the title compound, $C_5H_{11}N_2O^+\cdot C_4HO_4^-$, are connected by intermolecular N(amide)—$H\cdots$O(amide) hydrogen bonds into helical chains, whereas anions are interlinked by strong O(hydroxyl)—H$\cdots$O hydrogen bonds into chains. These two distinct chains are interconnected by both N(amide)—H$\cdots$O and N(ammonium)—H$\cdots$O hydrogen bonds into a three-dimensional framework. One of the ammonium protons is involved in a three-centre hydrogen bond.

Comment

In the course of our spectroscopic and structural studies of some optically active derivatives of amino acids having non-linear optical and electro-optical properties (Nalwa *et al.* 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987), the crystal structure of the title compound, L-prolinium amide hydrogensquarate (I), was determined. In addition, a vibrational spectroscopic study and the assignment of IR and Raman bands of (I) are reported. Structurally, (I) belongs to the C-amidated amino acids, whose salts and ester amides of squaric acid represent a new class of compounds of great biological importance. A structural study on the C-amidated amino acids Ile, Val, Thr, Ser, Met, Trp, Gln and Arg has been reported and the results compared with their C-unamidated counterparts (In *et al.*, 2001). A complete vibrational spectroscopic study of (I) has not been previously performed. Only normal Raman and surface-enhanced Raman spectroscopic experiments with thin-layer chromatography spots of L-proline using different laser excitation sources have been reported. The assignments were compared with those of polycrystalline samples (Istvan *et al.*, 2003). The conformational changes in oligomeric *N*-acyl-L-prolinate anions have also been studied by FTIR spectroscopy but no explicit vibrational analysis was carried out (Ishida *et al.*, 2001).



(I)

The asymmetric unit of (I) is depicted in Fig. 1. Translation-related hydrogensquarate anions are linked by strong intermolecular O3′—H3′$\cdots$O1′ hydrogen bonds [O3′$\cdots$O1′^{i} = 2.550 (2) Å and O3′—H3′$\cdots$O1′^{i} = 172.4°, symmetry code: (i) x, 1 + y, z] into infinite chains running parallel to the [010] direction. We have recently reported such unusual 1,3-

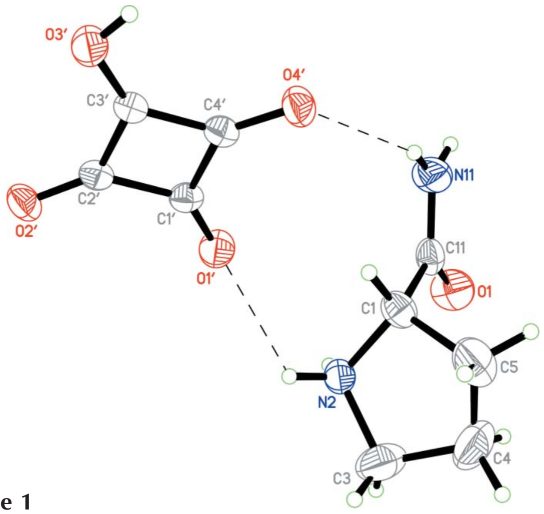


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

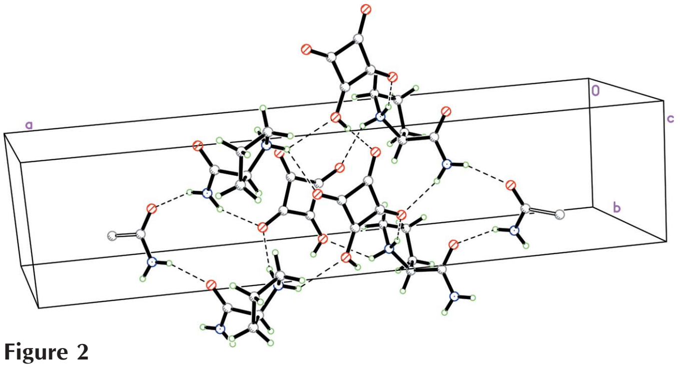


Figure 2
The crystal packing of (I) is characterized by a three-dimensional hydrogen-bonding (dashed lines) network.

hydrogen bonds between the hydrogensquarate hydroxyl group and a partially charged O atom (Kolev *et al.*, 2005) in the case of L-alaninium hydrogensquarate monohydrate. The alternate 3,4-hydrogen bonds are known, both in infinite chains (Angelova, Petrova *et al.*, 1996) and in dimers of hydrogensquarate anions (Angelova, Velikova *et al.*, 1996; Kolev *et al.*, 2004). All possible donor N—H bonds from the amide and ammonium groups of the prolinium cation participate in hydrogen bonds.

N—H⋯O interactions involving the amide N11 and O1 atoms (Table 1) link the prolinium cations into helical chains. These chains are connected to squarate chains by one N(amide)—H⋯O and three N(ammonium)—H⋯O hydrogen bonds, resulting in a three-dimensional framework (Table 1 and Fig. 2). A three-centre hydrogen bond between ammonium atom H22 and O3′ and O2′ of the anions is also involved in cation–anion connections.

Experimental

The starting compound L-proline amide was obtained as a white powder from Bachem (Switzerland) and recrystallized from methanol. Compound (I) was synthesized by adding a methanol solution (10 ml) of L-proline amide (114 mg) to an aqueous solution (14 ml) of squaric acid (114 mg). Colourless crystals, which formed after four weeks, were filtered off and dried in air at room temperature. Prismatic colourless single crystals, suitable for X-ray analysis, were grown from methanol–water (1:1) solution at room temperature over a period of two weeks. IR (KBr pellet) cm^{-1}: 3392 (*s*), 3187 (*sh*) ν (NH$_2$), 3018, 3050, 2881 ν (NH$_3$), 1815 (*w*) ν(C—O + C═O, hydrogensquarate), 1684 (*vs*) ν(C═O) (amide I), 1652 (NH$_2$, scissoring), 1631 δ(NH$_2$), 1582, 1499, 1449, 1349 δ(CH$_2$), 1386 ν(CN) (amide III), 1170, 1112, 934 ρ(NH$_3$) (rocks), 1136 ρ(NH$_2$) (rocks), 788 (amide VII), 722 ω(NH$_2$) + δ(C═O). Our assignment is in accordance with literature data (Ivanova, 2006*a*,*b*; Ivanova & Arnaudov, 2006) for a series of amino acids, peptides and amides as well as their Au^{III} complexes. Further special details of the IR assignment and the positions of the Raman bands are given as supplementary material in the CIF.

Crystal data

$C_5H_{11}N_2O^+ \cdot C_4HO_4^-$
M_r = 228.21
Monoclinic, *C*2
a = 25.904 (4) Å
b = 5.9781 (11) Å
c = 6.5805 (9) Å
β = 100.724 (17)°
V = 1001.3 (3) Å^3
Z = 4

D_x = 1.514 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 41 reflections
θ = 7.0–21.8°
μ = 0.13 mm^{-1}
T = 294 (2) K
Prism, colourless
0.55 × 0.32 × 0.24 mm

Data collection

Siemens P4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Sheldrick, 1995)
T_{min} = 0.856, T_{max} = 0.974
2233 measured reflections
950 independent reflections

926 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 25.0°
$h = -30 \rightarrow 30$
$k = -7 \rightarrow 1$
$l = -7 \rightarrow 7$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.09
950 reflections
146 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.5121P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.068 (11)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O3′—H3′⋯O1′^{i}	0.82	1.73	2.549 (3)	172
N2—H22⋯O2′^{ii}	0.90	2.23	2.904 (3)	132
N2—H22⋯O3′^{iii}	0.90	2.38	3.050 (3)	131
N2—H21⋯O4′^{iv}	0.90	1.97	2.829 (3)	160
N11—H11⋯O1^{v}	0.86	2.15	2.967 (2)	158
N11—H12⋯O4′^{vi}	0.86	2.20	2.968 (3)	148

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

In the absence of significant anomalous dispersion effects, Friedel pairs were merged. The *S* configuration of the L-prolinium amide α-carbon atom C1 is known for the natural amino acid and was assigned as such. The H atoms of the cation and anion were constrained to

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idealized positions and refined using a riding model, with C—H = 0.98 Å for the α-C atom C1 and 0.97 Å for the methylene C atoms C3–C5, N—H = 0.90 Å for the ammonium H atoms and 0.86 Å for the amide H, and O3′—H3′ = 0.82 Å for the hydrogensquarate hydroxyl group; $U_{\rm iso}$(H) values were set at 1.2$U_{\rm iso}$(C,N) and 1.5$U_{\rm iso}$(O3′).

Data collection: *R3m/V User's Guide* (Siemens, 1989); cell refinement: *R3m/V User's Guide*; 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* (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 Alexander von Humboldt Foundation and the Bulgarian National Fund for Research (grant X-1213).

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