L-Prolinium tartrate

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In the title salt, $C_5H_{10}NO_2^+ \cdot C_4H_5O_6^-$, proline exists as a cation and the tartaric acid as a semi-tartrate anion. The semi-tartrate ions form hydrogen-bonded strings along the c axis. These strings are interconnected through the proline molecules, forming a layered network parallel to the bc plane. The proline molecules, however, do not directly interact among themselves, except for a weak C—H···O hydrogen bond.

Comment

X-ray crystallographic investigations of the complexes of amino acids with carboxylic acids, being pursued in our laboratory, are aimed at understanding the nature of intermolecular interactions and biomolecular aggregation patterns that might well have occurred in prebiotic polymerization (Vijayan, 1988; Prasad & Vijayan, 1993). Recently, the crystal structure of sarcosinium tartrate has been elucidated and reported by Krishnakumar et al. (2001). The present study reports the crystal structure of the title salt, (I), a complex of L-proline with tartaric acid.

(I)
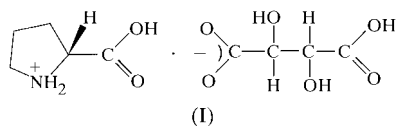
The proline molecule in (I) exists in the cationic form, with a positively charged amino group and an uncharged carboxylic acid group. The pyrrolidine ring adopts a conformation intermediate between an envelope and half-chair, as observed in L-proline monohydrate (Janczak & Luger, 1997), DL-proline monohydrate (Padmanabhan et al., 1995) and DL-proline hemisuccinic acid (Prasad & Vijayan, 1993). Atom C4 of the pyrrolidine ring exhibits positional disorder, with occupancy factors of 0.71 (1) and 0.29 (1) for C4 and C4′, respectively. This positional disorder may be due to the presence of a mixture of slightly different conformations of the pyrrolidine ring. In several other crystal structures containing proline, atom C4 exhibits a higher displacement parameter, although in none of them has disorder been observed.

The pyrrolidine ring is nearly planar [mean deviation 0.140 (3) Å] and atom C4 (C^γ) is in a cis position, as observed

in the crystal structure of L-proline (Kayushina & Vainshtein, 1966). However, the disordered component, C4′, is in a trans position with respect to the carboxyl group. The angle between the plane of the carboxyl group and the pyrrolidine ring is 70.1 (2)°.
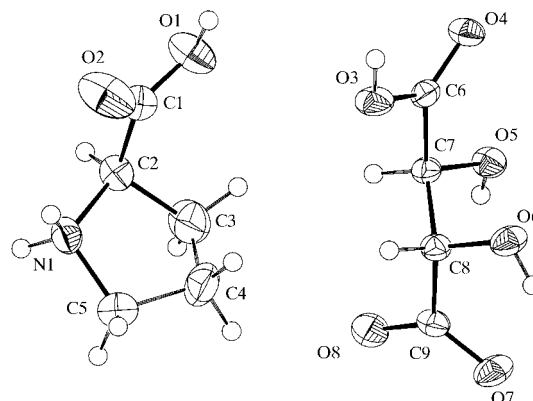

Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are at the 50% probablity level and H atoms are shown as small spheres of arbitrary radii. Only the major disordered component of C4 is shown.

The tartaric acid molecule exists as a semi-tartrate ion, with an uncharged carboxyl group and a carboxylate ion. The angle between the planes of the half-molecules is 71.4 (1)°, which is higher than the values of 54.6 (4) and 65.0 (1)° found in the structures of tartaric acid (Okaya et al., 1966) and sarcosinium tartrate (Krishnakumar et al., 2001), respectively. The carbon backbone of the semi-tartrate ion is planar.

The crystal structure (Fig. 2) is stabilized by hydrogen bonds (Table 1). The amino acid molecules do not directly interact among themselves, except for the presence of a weak C—H···O hydrogen bond. The semi-tartrate ions form hydrogen-bonded strings along the c axis and are interconnected through proline molecules, forming a layered network parallel to the bc plane. This aggregation pattern is similar to that observed in the crystal structure of sarcosinium tartrate (Krishnakumar et al., 2001).
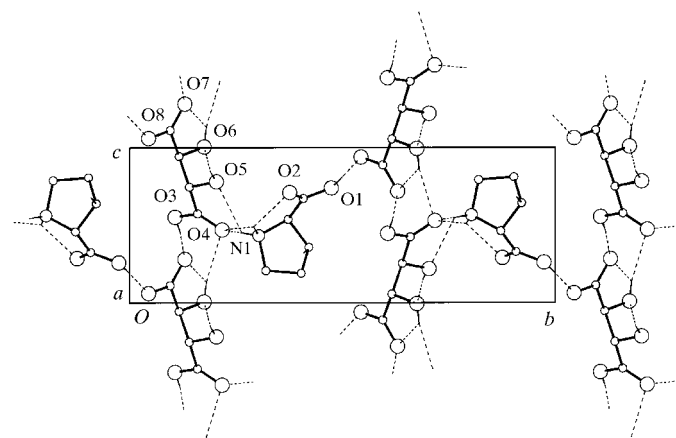

Figure 2
The packing diagram of the structure of (I) viewed down the a axis.

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organic compounds

Experimental

Colourless single crystals of salt (I) were grown as transparent needles from a saturated aqueous solution containing L-proline and tartaric acid in a stoichiometric ratio. The density was determined by the flotation method using a liquid mixture of carbon tetrachloride and xylene.

Crystal data

$C_5H_{10}NO_2{}^+ \cdot C_4H_5O_6{}^-$
$M_r = 267.24$
Monoclinic, $P2_1$
$a = 5.007\,(1)$ Å
$b = 17.676\,(3)$ Å
$c = 6.523\,(1)$ Å
$\beta = 100.40\,(2)°$
$V = 567.8\,(2)$ Å^3
$Z = 2$
$D_x = 1.551$ Mg m^{-3}

$D_m = 1.55$ Mg m^{-3}
D_m measured by flotation
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 16–26°$
$\mu = 1.207$ mm^{-1}
$T = 293\,(2)$ K
Needle, colourless
$0.42 \times 0.35 \times 0.21$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North et al., 1968)
$T_{min} = 0.540$, $T_{max} = 0.734$
1077 measured reflections
974 independent reflections
968 reflections with $I > 2\sigma(I)$

$R_{int} = 0.018$
$\theta_{max} = 67.9°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 17$
$l = -7 \rightarrow 6$
2 standard reflections
   every 200 reflections
   intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.04$
974 reflections
178 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o{}^2) + (0.0513P)^2 + 0.1468P]$
  where $P = (F_o{}^2 + 2F_c{}^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.060 (4)

All H atoms were located from a difference Fourier map and were allowed to ride on their parent atoms, with C—H = 0.97–0.98, N—H = 0.90 and O—H = 0.82 Å. The absolute configuration of this light-atom structure was not established by the analysis but is known from the configuration of the starting reagents.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*93 (Sheldrick, 1990);

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1$\cdots$O8^i	0.82	1.72	2.531 (3)	170
N1—H9$\cdots$O4^{ii}	0.90	2.21	2.994 (3)	146
N1—H10$\cdots$O4^{iii}	0.90	2.06	2.881 (3)	152
O3—H11$\cdots$O7^i	0.82	1.68	2.490 (2)	171
O5—H13$\cdots$O6^{iv}	0.82	2.14	2.954 (2)	170
O6—H15$\cdots$O4^v	0.82	2.31	3.105 (3)	162
C2—H2$\cdots$O2^{iv}	0.98	2.23	3.112 (3)	149

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

program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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