organic papers

L-Alaninium tartrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.044
wR factor = 0.114
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.

In the title compound, $C_3H_8NO_2{}^+ \cdot C_4H_5O_6{}^-$, the L-alanine molecule exists in the cationic form, with a positively charged amino group and an uncharged carboxylic acid group. The tartaric acid molecule exists in the mono-ionized state. The structure is stabilized by a three-dimensional network of O—H⋯O and N—H⋯O hydrogen bonds. No head-to-tail hydrogen bond is observed among the amino acid molecules. The aggregation pattern observed in the structure has striking similarities to those observed in other related amino acid–tartaric acid complexes.

Comment

Precise X-ray crystallographic investigations of amino acid–carboxylic acid complexes are expected to throw much light on 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 structures of sarcosinium tartrate (Krishnakumar *et al.*, 2001) and L-prolinium tartrate (Subha Nandhini *et al.*, 2001) have been elucidated in our laboratory. The present study reports the crystal structure of the title compound, (I), a complex of L-alanine with tartaric acid.
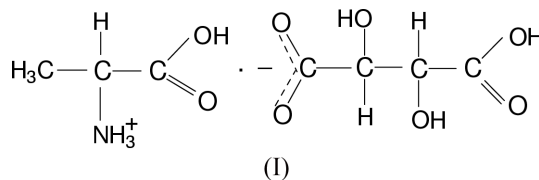

(I)

Fig. 1 shows the molecular structure of (I), with the atom-numbering scheme. The L-alanine molecule in (I) exists in the cationic form, with a positively charged amino group and an uncharged carboxylic acid group. The tartaric acid molecule exists as a semi-tartrate ion, with a free carboxylic acid group and a negatively charged carboxylate ion. The C4—O3 and C4=O4 bond distances [1.279 (4) and 1.238 (4) Å, respectively] of the free carboxylic acid group are significantly different from, but closely related to, those of sarcosinium tartrate [1.288 (3) and 1.222 (3) Å, respectively] and L-prolinium tartrate [1.294 (4) and 1.200 (4) Å, respectively]. The decrease in the C—O and increase in the C=O bond lengths may be attributed to a strong O3—H3⋯O8(x, y, z + 1) hydrogen bond observed in the crystal structure, with an O⋯O distance of 2.466 (3) Å. This observation is supported by the fact that strong O—H⋯X hydrogen bonds involving the carboxylic acid O atom as donor permit some double-bond character in the C—O bond and some single-bond character in C=O (Hahn, 1957). The angle between the planes of the two
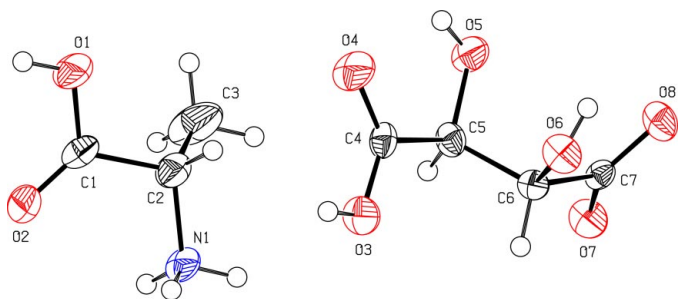
Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.
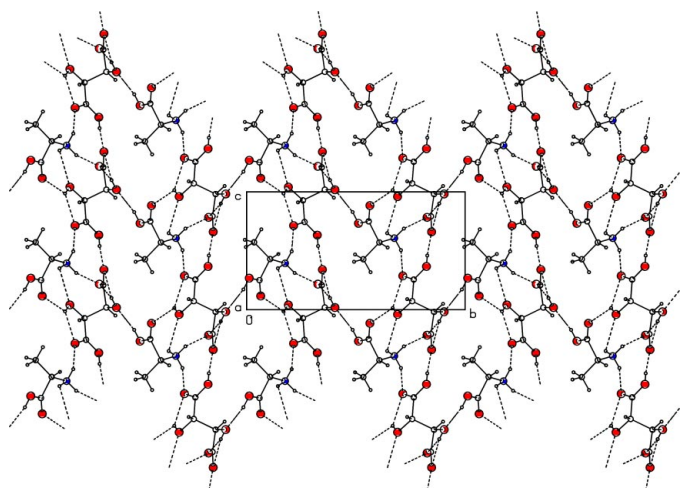

Figure 2
The packing of molecules of (I), viewed down the *a* axis.

halves of the semi-tartrate ion, O3/O4/C4/C5/O5 and O7/O8/C6/C7/O6, is 53.0 (1)°, which agrees well with the value observed in tartaric acid [54.6 (4)°; Okaya *et al.*, 1966], but deviates far from the values observed in sarcosinium tartrate [65.0 (1)°; Krishnakumar *et al.*, 2001] and L-prolinium tartrate [71.4 (1)°; Subha Nandhini *et al.*, 2001]. The carbon skeleton of the semi-tartrate anion is essentially planar [torsion angle C4—C5—C6—C7 −175.1 (2)°]. The C—O double- and single-bond distances of the carboxylic acid group of the amino acid molecule are found to be as expected [1.185 (5) and 1.319 (5) Å, respectively].
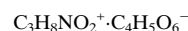
Fig. 2 shows the packing of molecules of (I), viewed down the shortest axis (*a* axis). The alaninium and semi-tartrate ions form alternate layers along the *c* axis. No head-to-tail hydrogen bond is observed among the amino acid molecules, as in the cases of sarcosinium tartrate (Krishnakumar *et al.*, 2001) and L-prolinium tartrate (Subha Nandhini *et al.*, 2001). Alaninium and semi-tartrate ions aggregate into layers parallel to the *ac* plane. These layers are interconnected by the translation-related O—H···O and N—H···O hydrogen bonds, leading to a characteristic three-dimensional aggregation pattern. Semi-tartrate anions are held together by the translation-related O—H···O hydrogen bonds. A common feature observed among the crystal structures of (I), sarcosi-

nium tartrate and L-prolinium tartrate is that the shortest cell dimension in all of them is close to 5.0 Å. The aggregation pattern observed in (I) has striking similarities to those observed in the other two amino acid–tartaric acid complexes. Interestingly, in all the amino acid–tartaric acid complexes studied so far, no direct hydrogen-bonded links are observed among the amino acid molecules.

Experimental

Colorless plate-shaped single crystals of (I) were grown from a saturated aqueous solution containing L-alanine and tartaric acid in a 1:1 ratio.

Crystal data

$C_3H_8NO_2^+ \cdot C_4H_5O_6^-$	D_m measured by flotation in a
$M_r = 239.18$	mixture of xylene and carbon
Monoclinic, $P2_1$	tetrachloride
$a = 5.1446$ (8) Å	Mo $K\alpha$ radiation
$b = 13.721$ (3) Å	Cell parameters from 25
$c = 7.4751$ (9) Å	reflections
$\beta = 98.09$ (1)°	$\theta = 2.8$–25.0°
$V = 522.42$ (14) Å^3	$\mu = 0.14$ mm^{-1}
$Z = 2$	$T = 293$ (2) K
$D_x = 1.521$ Mg m^{-3}	Plate, colorless
$D_m = 1.53$ Mg m^{-3}	$0.35 \times 0.30 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.018$
diffractometer	$\theta_{max} = 25.0°$
ω–2θ scans	$h = 0 \rightarrow 6$
Absorption correction: ψ scan	$k = 0 \rightarrow 16$
(North *et al.*, 1968)	$l = -8 \rightarrow 8$
$T_{min} = 0.952$, $T_{max} = 0.979$	2 standard reflections
1061 measured reflections	every 200 reflections
954 independent reflections	intensity decay: <2%
944 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 0.196P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
954 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
146 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.045 (14)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.319 (5)	O8—C7	1.256 (4)
O2—C1	1.185 (5)	N1—C2	1.479 (5)
O4—C4	1.238 (4)	C1—C2	1.533 (5)
O7—C7	1.247 (4)	C2—C3	1.503 (6)
O2—C1—O1	125.4 (3)	N1—C2—C1	107.8 (3)
O2—C1—C2	124.5 (3)	C3—C2—C1	111.8 (4)
O1—C1—C2	110.1 (3)	O7—C7—O8	125.5 (3)
N1—C2—C3	111.9 (4)		
O2—C1—C2—N1	−10.8 (5)	O4—C4—C5—O5	0.4 (4)
O1—C1—C2—N1	167.7 (3)	C4—C5—C6—C7	−175.1 (2)
O2—C1—C2—C3	112.5 (5)	O6—C6—C7—O8	−19.5 (4)
O1—C1—C2—C3	−69.0 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O6^i	0.82	1.84	2.651 (4)	169
O6—H6···O7^{ii}	0.82	1.99	2.765 (4)	158
O5—H5···O4	0.82	2.15	2.639 (3)	119
O5—H5···O2^{ii}	0.82	2.34	2.878 (4)	124
O3—H3···O8^{iii}	0.82	1.66	2.466 (3)	170
N1—H1A···O7	0.89	1.90	2.740 (4)	157
N1—H1C···O5^{iv}	0.89	2.49	2.958 (4)	114
N1—H1B···O4^v	0.89	2.01	2.815 (4)	149

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

In the absence of significant anomalous scattering effects and with no Friedel pairs, the absolute configuration, assumed from the synthesis, could not be confirmed crystallographically. The positions of H atoms, located from the final difference Fourier map, were in disagreement with those favoured by the dimensions of the carboxyl and carboxylate groups of the tartrate anion. Hence, H atoms were generated geometrically and were allowed to ride on their respective parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults for bond lengths and displacement parameters.

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*97 (Sheldrick, 1990); 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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