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DL-Alaninium oxalate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.126
Data-to-parameter ratio = 12.4

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

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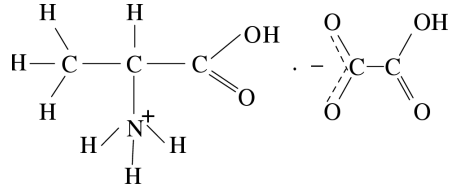
In the title compound, $C_3H_8NO_2^+\cdot C_2HO_4^-$, the alanine molecule exists in the protonated cationic form and the oxalic acid molecule in the mono-ionized state. The alanine molecules dimerize across inversion centres through head-to-tail N—H···O hydrogen bonds. The semi-oxalate ions aggregate into hydrogen-bonded strings along the shortest cell axis. The crystal structure is also characterized by the presence of a C—H···O hydrogen bond and a short C···O contact between amino acids.

Comment

X-ray crystallographic investigations of the complexes of amino acids with carboxylic acids are expected to throw light on the nature of intermolecular interactions and biomolecular aggregation patterns that might have occurred in prebiotic polymerization (Vijayan, 1988; Prasad & Vijayan, 1993). Recently, an accurate determination of the crystal structure of DL-alanine (Subha Nandhini *et al.*, 2001*b*) was carried out in our laboratory. The present study reports the crystal structure of the title salt, (I), a complex of DL-alanine with oxalic acid.



(I)

Fig. 1 shows the molecular numbering scheme. The amino acid molecule exists in the cationic form with a neutral carboxylic acid group and a protonated amino group. The oxalic acid molecule exists in the mono-ionized state. In the asymmetric unit, the DL-alaninium cation and the semi-oxalate anion are linked to each other through a N—H···O hydrogen bond. The conformation of the DL-alaninium ions in the present structure is significantly different from the values observed for DL-alanine. The N atom deviates by 0.148 (4) Å from the carboxylate plane and the methyl C atom deviates by 1.063 (5) Å in the opposite direction. The corresponding values observed in DL-alanine are 0.392 (5) and 1.356 (4) Å, respectively. The conformation of the semi-oxalate ion remains essentially planar as observed in the crystal structures of other complexes of amino acids with oxalic acid.

In the crystal structure of (I), the alanine molecules dimerize across inversion centres through head-to-tail N—

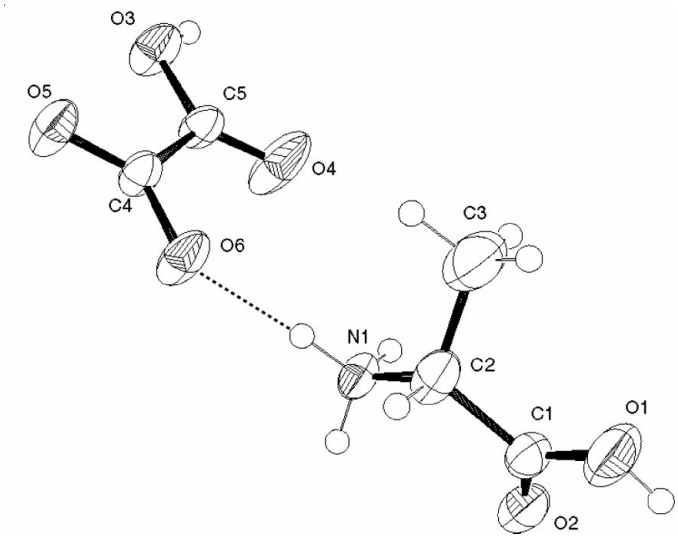


Figure 1
The molecular structure of (I) with atom-numbering scheme and 50% probability displacement ellipsoids.

H···O hydrogen bonds, as observed in many other amino acid racemates (Soman & Vijayan, 1989). The hydrogen-bonded alanine dimers form columns along the *b* axis and each such column is connected to others through semi-oxalate ions (Fig. 2). The semi-oxalate ions aggregate into hydrogen-bonded strings along the shortest cell axis, generated by translation as observed in glycinium oxalate (Subha Nandhini *et al.*, 2001*a*) and L-alaninium oxalate (Subha Nandhini *et al.*, 2001*c*). The crystal structure is also characterized by the presence of a C—H···O hydrogen bond and a short C···O contact [C1···O2($-x+2$, $-y+1$, $-z+1$) = 2.987 (6) Å] between amino acids. While the aggregation pattern of the semi-oxalate ions is identical in the crystal structures of oxalic acid complexes of glycine, L-alanine and the title compound, (I), the aggregation of amino acid molecules shows no common pattern.

Experimental

Crystals of (I) were grown from a saturated aqueous solution containing DL-alanine and oxalic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_3H_8NO_2^+\cdot C_2HO_4^-$
M_r = 179.13
Monoclinic, $P2_1/n$
a = 5.662 (2) Å
b = 7.342 (2) Å
c = 19.157 (6) Å
β = 94.48 (3)°
V = 793.9 (4) Å^3
Z = 4
D_x = 1.499 Mg m^{-3}
D_m = 1.50 Mg m^{-3}
D_m measured by flotation in a mixture of xylene and bromoform
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 6–14°
μ = 0.14 mm^{-1}
T = 293 (2) K
Needle, colourless
0.48 × 0.32 × 0.22 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.89, T_{max} = 0.97
1542 measured reflections
1390 independent reflections
1103 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 24.9°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 8$
$l = -22 \rightarrow 22$
2 standard reflections
frequency: 60 min
intensity decay: 0.1%

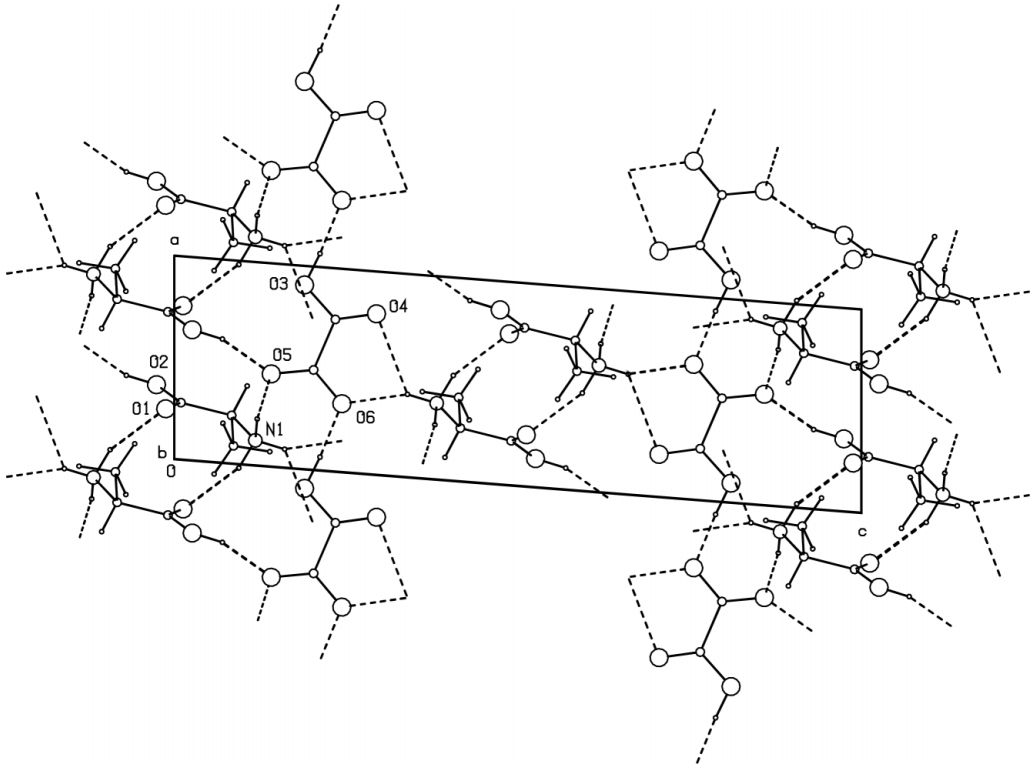


Figure 2
Packing diagram of the molecules of (I) in the unit cell viewed down the *b* axis.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.5084P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.126$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
$S = 1.12$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
1390 reflections	Extinction correction: *SHELXL*97
112 parameters	Extinction coefficient: 0.016 (4)
H-atom parameters constrained	

Table 1
Selected torsion angles (°).

O2—C1—C2—N1	−6.2 (3)	O2—C1—C2—C3	−129.1 (3)
O1—C1—C2—N1	174.0 (2)	O1—C1—C2—C3	51.0 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O5^{i}	0.82	1.80	2.591 (2)	161
O3—H3···O6^{ii}	0.82	1.77	2.587 (2)	174
N1—H1*A*···O5^{iii}	0.89	1.98	2.834 (3)	161
N1—H1*B*···O2^{iv}	0.89	2.03	2.863 (3)	154
N1—H1*C*···O6	0.89	1.96	2.818 (2)	162
C2—H2···O4^{v}	0.98	2.53	3.423 (3)	152

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

H atoms were placed in calculated positions and were allowed to ride on their parent atoms with HFIX instructions using *SHELXL*97 defaults (Sheldrick, 1997).

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, 1997); 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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