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L-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 = 0.030
wR factor = 0.083
Data-to-parameter ratio = 7.8

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

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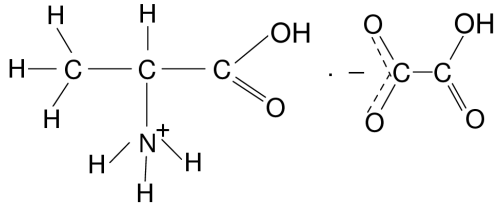
In the title compound, $C_3H_8NO_2^+\cdot C_2HO_4^-$, the alanine molecule exists in the cationic form and the oxalic acid molecule in the mono-ionized state. The alaninium and semi-oxalate ions form alternate columns leading to a layered arrangement parallel to the *ac* plane and each such layer is interconnected to the other through N—H···O hydrogen bonds. The overall aggregation pattern is distinctly different from that observed in the glycine–oxalic acid complex.

Comment

X-ray studies on crystalline complexes of amino acids with carboxylic acids have provided a wealth of information regarding intermolecular interactions and biomolecular aggregation patterns (Vijayan, 1988; Prasad & Vijayan, 1993). The crystal structures of glycinium oxalate (Subha Nandhini *et al.*, 2001) and sarcosinium oxalate monohydrate (Krishnakumar *et al.*, 1999) were elucidated in our laboratory. The present study reports the crystal structure of L-alaninium oxalate, (I), as part of a series of investigations being carried out to observe conformational changes in amino acid molecules and characteristic hydrogen-bonding patterns in their crystal structures.



(I)

Fig. 1 shows the molecular structure with the numbering scheme. The alanine molecule exists in the cationic form with a protonated amino group and an uncharged carboxylic acid group. The oxalic acid molecule exists in a mono-ionized state. The conformation of the L-alaninium cation about the N—C^{α} bond corresponds to the staggered ethane-type. A common feature between the crystal structures of glycinium oxalate and (I) is that the shortest cell dimensions are similar, 5.650 (2) and 5.6304 (15) Å, respectively. The semi-oxalate ions form hydrogen-bonded strings along the shortest cell axis, generated by translation, as in the structures of oxalic acid complexes of glycine (Subha Nandhini *et al.*, 2001) and lysine (Venkatraman *et al.*, 1997).

In the asymmetric unit, the L-alaninium cation and the semi-oxalate anion are linked to each other through a N—H···O hydrogen bond (Fig. 1). The head-to-tail hydrogen bond, with

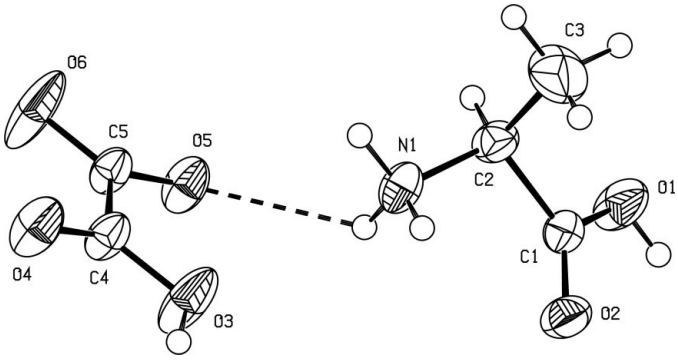


Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids.

O2 of the carboxyl group as acceptor, observed among the amino acid molecules in the crystal structure may be described as a zigzag sequence along the 2_1 screw axis along the direction of the *a* axis. The alaninium and semi-oxalate ions form alternate columns leading to a layered arrangement parallel to the *ac* plane and each such layer is interconnected to the other through N—H···O hydrogen bonds. Two short C···O contacts involving the carboxyl oxygen of the alaninium ion [C1···O2($-\frac{1}{2}+x$, $\frac{3}{2}-y$, $-z$) = 2.931 (3) Å and C2···O2($-\frac{1}{2}+x, \frac{3}{2}-y, -z$) = 2.977 (3) Å] are also observed in these layers. The slight difference observed in the bond lengths of C5—O5 and C5—O6 in the carboxylate group of the semi-oxalate ion may be attributed to the difference in the strengths of the N—H···O hydrogen bonds in which both O5 and O6 are involved (Table 2). The overall aggregation pattern is distinctly different from that observed in the glycine–oxalic acid complex.

Experimental

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

Crystal data

$C_3H_8NO_2^+\cdot C_2HO_4^-$
M_r = 179.13
Orthorhombic, $P2_12_12_1$
a = 5.6304 (15) Å
b = 7.2353 (15) Å
c = 19.597 (3) Å
V = 798.3 (2) Å^3
Z = 4
D_x = 1.490 Mg m^{-3}
D_m = 1.49 Mg m^{-3}

D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 4–68°
μ = 1.23 mm^{-1}
T = 293 (2) K
Needle, colourless
0.20 × 0.15 × 0.11 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.79, T_{max} = 0.87
879 measured reflections
879 independent reflections
853 reflections with $I > 2\sigma(I)$

θ_{max} = 67.9°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 23$
2 standard reflections
every 25 reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.09
879 reflections
112 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.1739P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.040 (3)
Absolute structure: see below

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.483 (3)	O5—C5	1.219 (2)
O1—C1	1.303 (2)	O6—C5	1.235 (2)
O2—C1	1.205 (2)	C1—C2	1.508 (3)
O3—C4	1.297 (2)	C2—C3	1.522 (3)
O4—C4	1.199 (2)	C4—C5	1.548 (3)
O2—C1—C2—N1	−29.3 (3)	O2—C1—C2—C3	90.4 (3)
O1—C1—C2—N1	153.29 (18)	O1—C1—C2—C3	−87.0 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O6^{i}	0.89	1.91	2.728 (2)	152
N1—H1B···O4^{ii}	0.89	2.28	3.085 (2)	150
N1—H1C···O2^{iii}	0.89	2.30	2.978 (2)	133
N1—H1C···O5	0.89	2.35	2.896 (2)	120
O1—H1···O5^{iv}	0.82	1.76	2.575 (2)	170
O3—H3···O6^{v}	0.82	1.73	2.545 (2)	172

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

The absolute structure of (I) was not established by the analysis but is known from the configuration of the starting reagents. The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms with *HFIX* instructions using *SHELXL*97 (Sheldrick, 1997) defaults.

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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