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Bis(DL-aspartic acid) oxalate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.193
Data-to-parameter ratio = 19.6

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

In the title compound, $2C_4H_8NO_4^+\cdot C_2O_4^{2-}$, the amino acid molecule exists in the cationic form and the oxalic acid molecule exists as a doubly charged oxalate anion which lies across an inversion centre in the crystal. The screw-related cations are linked by N—H···O hydrogen bonds to form infinite columns parallel to the b axis. The columns are interlinked by anions through O—H···O and N—H···O hydrogen bonds, forming a three-dimensional network.

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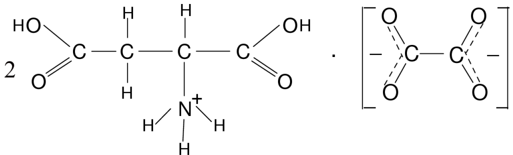
Comment

Aspartic acid, considered a non-essential amino acid, plays a paramount role in metabolism during construction of other amino acids and biochemicals in the citric acid cycle. The present study, which reports the crystal structure of a complex of DL-aspartic acid with oxalic acid, (I), forms part of a series of X-ray investigations being carried out in our laboratory on amino acid–carboxylic acid complexes. Precise X-ray investigations on these complexes have revealed interesting and useful data regarding the ionization states of individual molecules, their stoichiometry and intermolecular aggregation patterns. Recently, the crystal structures of glycinium oxalate (Subha Nandhini *et al.*, 2001*a*), L-and DL-alaninium oxalate (Subha Nandhini *et al.*, 2001*b*,*c*), DL-threoninium oxalate (Subha Nandhini *et al.*, 2001), β-alaninium oxalate (Krishnakumar *et al.*, 2002) and bis(serinium) oxalate dihydrate (Alagar *et al.*, 2002) were reported from our laboratory.



(I)

Fig. 1 shows the molecular structure of (I), with the atom-numbering scheme. The amino acid molecule exists in the expected cationic form with a positively charged amino group and protonated carboxylic acid groups. Interestingly, although complexes of racemic (DL-) amino acids with oxalic acid reported so far have crystallized in a variety of space groups, the values of their shortest cell dimensions all lie around 5.5 Å. The main chain torsion angle (C1—C2—C3—C4) has a value of −66.7 (3)°, significantly different from the value of 174.2 (2)° observed in the neutron diffraction study of DL-aspartic acid (Sequeira *et al.*, 1989). The oxalic acid molecule exists as a doubly charged oxalate anion (uncommon in similar crystal structures) and lies across an inversion centre in the crystal; its charge contribution to the asymmetric unit is

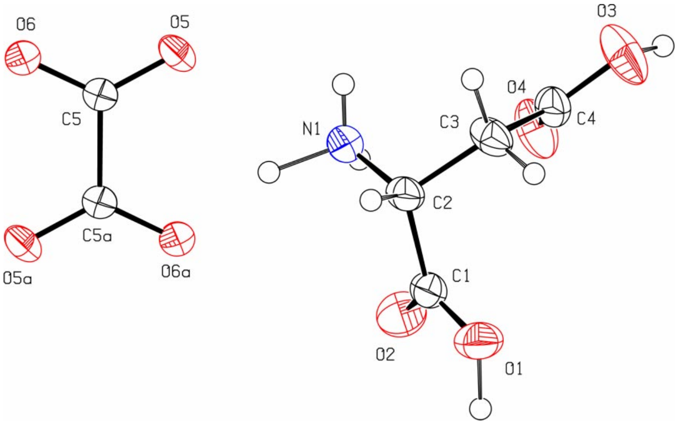


Figure 1
The cation and the complete anion of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. Atoms with suffix a are generated by inversion.

−1. Thus, one amino acid cation and half an oxalate anion are present in the asymmetric unit, leading to a 2:1 stoichiometry.

Fig. 2 shows the packing of the molecules of (I), viewed down the *b* axis. Each of the carboxylate O atoms of the oxalate anion participates in the hydrogen bonding as an acceptor of two hydrogen bonds. The screw-related aspartic acid cations are linked by N—H⋯O hydrogen bonds to form infinite column-like structures, parallel to the *b* axis. These molecular columns are interlinked by oxalate anions through O—H⋯O and N—H⋯O hydrogen bonds, forming a three-dimensional network (Fig. 2). The aggregation of individual molecules observed in the present structure differs distinctly from other amino acid–carboxylic acid structures and has some resemblance to the complex of oxalic acid with serine.

Experimental

Colorless needle-shaped single crystals of (I) were grown from a saturated aqueous solution containing DL-aspartic acid and oxalic acid in a 1:1 stoichiometric ratio.

Crystal data

$2C_4H_8NO_4^+\cdot C_2O_4^{2-}$
$M_r = 356.24$
Monoclinic, $P2_1/n$
$a = 7.387$ (1) Å
$b = 5.477$ (1) Å
$c = 18.522$ (3) Å
$\beta = 99.36$ (1)°
$V = 739.4$ (2) Å^3
$Z = 2$
$D_x = 1.600$ Mg m^{-3}
$D_m = 1.61$ Mg m^{-3}
D_m measured by flotation in a mixture of xylene and bromoform
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 39.3$–$39.8°$
$\mu = 0.15$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.24 × 0.22 × 0.12 mm

Data collection

Rigaku *AFC*-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.89$, $T_{\max} = 0.99$
2321 measured reflections
2171 independent reflections
1191 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 30.1°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 7$
$l = -26 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: none

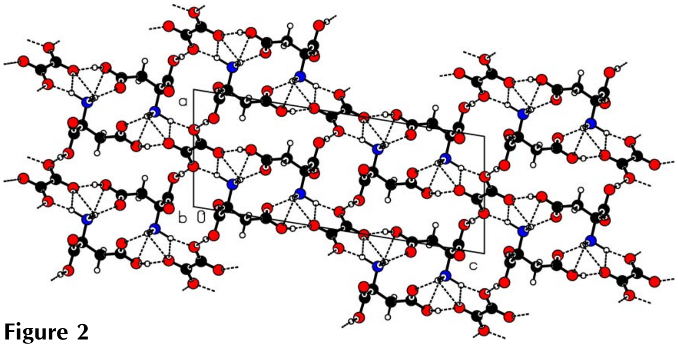


Figure 2
The packing of (I), viewed down the *b* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.193$
$S = 1.04$
2171 reflections
111 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0959P)^2 + 0.3684P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯O6$^{\rm i}$	0.82	1.71	2.530 (3)	178
O3—H3⋯O5$^{\rm ii}$	0.82	1.75	2.565 (2)	179
N1—H1*A*⋯O4$^{\rm iii}$	0.89	2.08	2.822 (3)	140
N1—H1*B*⋯O4	0.89	2.26	2.855 (3)	124
N1—H1*C*⋯O6$^{\rm iv}$	0.89	1.88	2.733 (3)	160

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

All H atoms were positioned geometrically and were allowed to ride on their respective parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults for bond lengths and displacement parameters. Rotating-group refinement was used for the —OH groups.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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