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#### Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
 R factor = 0.045  
 wR factor = 0.117  
 Data-to-parameter ratio = 7.4

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

## L-Leucinium oxalate

In the title compound,  $\text{C}_6\text{H}_{14}\text{NO}_2^+\cdot\text{C}_2\text{HO}_4^-$ , the leucine molecule exists in the cationic form, with a protonated amino group and an uncharged carboxylic acid group. Oxalic acid exists in the mono-ionized state. Pseudo-inversion centres relate the leucinium cations and semi-oxalate anions. The leucinium and semi-oxalate ions form hydrogen-bonded, double-layered chains, extending parallel to the *b* axis. The leucinium cations are arranged in these double layers on opposite sides leading to alternating hydrophobic and hydrophilic layers.

#### Comment

Leucine is one of the most important amino acids, essential for the growth and maintenance of living organisms. Simple carboxylic acids, which are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971), form crystalline complexes with amino acids. The structure elucidation of the title compound, (I), was undertaken as part of a programme of research on complexes of amino acids with dicarboxylic acids. This research in our laboratory aims to study the nature of intermolecular interactions and characteristic aggregation patterns, at atomic resolution. Recently, the crystal structures of sarcosinium oxalate monohydrate (Krishnakumar *et al.*, 1999), glycinium oxalate (Subha Nandhini *et al.*, 2001a), L- and DL-alaninium oxalate (Subha Nandhini *et al.*, 2001b,c), DL-threoninium oxalate (Subha Nandhini *et al.*, 2001),  $\beta$ -alaninium oxalate (Krishnakumar *et al.*, 2002), bis(DL-serinium) oxalate dihydrate (Alagar *et al.*, 2002) and bis(DL-aspartic acid) oxalate (Alagar *et al.*, 2003) have been reported from our laboratory.

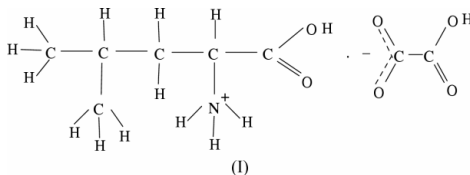
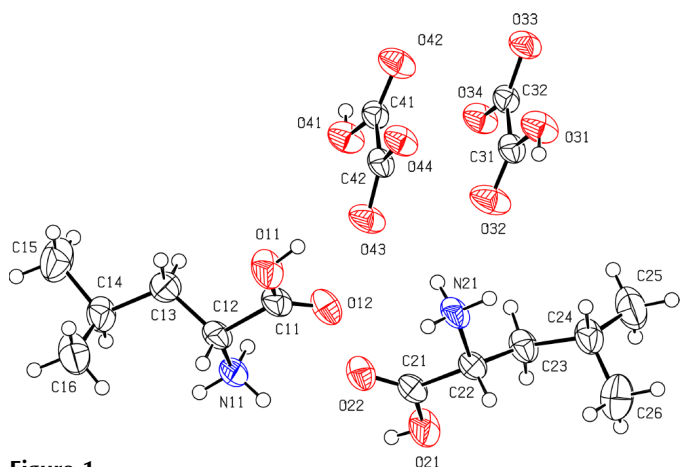


Fig. 1 shows the molecular structure with the atom-numbering scheme. The asymmetric unit contains two leucinium cations and two semi-oxalate anions; the former have protonated amino groups and uncharged carboxylic acid groups, the latter each have a neutral carboxylic acid group and a negatively charged carboxylate group. The two cations exhibit significant differences in conformation, as do the two anions (Table 1; corresponding angles are listed side-by-side). The semi-oxalate ions are related to each other through a pseudo-inversion centre. Interestingly, the two leucinium

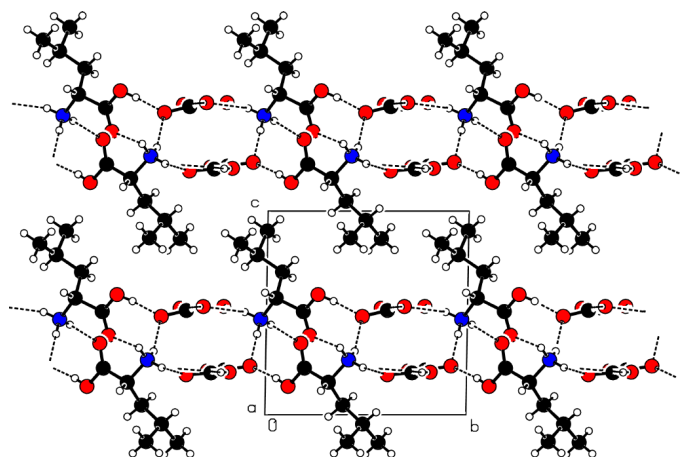
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**Figure 1**  
The asymmetric unit of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.



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

cations are also related by a pseudo-inversion centre, ignoring the side chain C atoms. A feature common to the crystal structures of glycinium oxalate, L-alaninium oxalate and (I) is that the shortest cell dimensions are similar, *viz.* 5.650 (2), 5.630 (1) and 5.674 (3) Å, respectively.

Fig. 2 shows the packing of the molecules of (I), viewed down the *a* axis. The leucinium and semi-oxalate ions are linked to each other through N—H···O and O—H···O hydrogen bonds. Head-to-tail hydrogen bonds, of type S2, with O12 and O22 of the carboxylic groups as acceptors are present in the structure. The semi-oxalate ions are interconnected by direct O—H···O interactions, forming hydrogen-bonded strings along the shortest cell axis, as observed in many other amino acid–oxalic acid complexes. The leucinium and semi-oxalate ions form hydrogen-bonded double layers. The leucinium cations are arranged in these double layers on opposite sides, leading to alternating hydrophobic and hydrophilic layers. These layers are held together, in addition to van der Waals interactions, by a few short contacts O12···O22(*x* + 1, *y*, *z*) = 2.893 (4) Å; a carbonyl–carbonyl contact O22···C11(*x* − 1, *y*, *z*) = 2.989 (5) Å (Allen *et al.*, 1998) and C31···C41 = 3.164 (5) Å. The C—C bond lengths of

the semi-oxalate anions, C31—C32 = 1.546 (4) Å and C41—C42 = 1.543 (4) Å, are slightly larger and may be justified by intramolecular O···O steric hindrance. Similar large deviations from normally expected values in C—C bond lengths are also observed in the case of oxalic acid dihydrate (1.537 Å; Ahmed & Cruickshank, 1953) and in the crystal structures of anhydrous  $\alpha$ - and  $\beta$ -oxalic acids [1.537 (1) and 1.537 (1) Å, respectively; Derissen & Smith, 1974].

## Experimental

Colourless plate-shaped single crystals of (I) were grown from a saturated aqueous solution containing L-leucine and oxalic acid in a stoichiometric ratio of 1:1.

### Crystal data

$C_6H_{14}NO_2^+ \cdot C_2HO_4^-$   
 $M_r = 221.21$   
 Triclinic, *P1*  
 $a = 5.674$  (3) Å  
 $b = 9.803$  (9) Å  
 $c = 9.906$  (8) Å  
 $\alpha = 87.37$  (7)°  
 $\beta = 99.64$  (5)°  
 $\gamma = 100.35$  (6)°  
 $V = 534.3$  (7) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.375$  Mg m<sup>−3</sup>

$D_m = 1.39$  (3) Mg m<sup>−3</sup>  
 $D_m$  measured by flotation in a mixture of xylene and CCl<sub>4</sub>  
 Cu  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 2.8$ –72°  
 $\mu = 1.02$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
 Plate, colourless  
 0.35 × 0.20 × 0.15 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ –2 $\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{min} = 0.773$ ,  $T_{max} = 0.858$   
 2223 measured reflections  
 2003 independent reflections  
 1866 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.045$   
 $\theta_{max} = 72.0^\circ$   
 $h = -4 \rightarrow 6$   
 $k = -12 \rightarrow 11$   
 $l = -12 \rightarrow 12$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: <2%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.117$   
 $S = 1.04$   
 2003 reflections  
 272 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0934P)^2 + 0.031P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.27$  e Å<sup>−3</sup>  
 $\Delta\rho_{min} = -0.26$  e Å<sup>−3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.024 (5)

**Table 1**

Selected geometric parameters (°).

O12—C11—C12—N11	0.6 (4)	O22—C21—C22—N21	−12.2 (4)
O11—C11—C12—N11	−178.3 (3)	O21—C21—C22—N21	169.6 (3)
O12—C11—C12—C13	−121.4 (3)	O22—C21—C22—C23	−135.9 (3)
O11—C11—C12—C13	59.7 (4)	O21—C21—C22—C23	45.9 (4)
N11—C12—C13—C14	66.4 (4)	N21—C22—C23—C24	71.3 (4)
C11—C12—C13—C14	−174.0 (3)	C21—C22—C23—C24	−167.2 (3)
C12—C13—C14—C16	60.5 (4)	C22—C23—C24—C25	−171.7 (3)
C12—C13—C14—C15	−176.2 (3)	C22—C23—C24—C26	66.0 (4)
O32—C31—C32—O33	175.0 (3)	O42—C41—C42—O43	−168.5 (3)
O31—C31—C32—O33	−3.0 (4)	O41—C41—C42—O43	10.1 (4)
O32—C31—C32—O34	−3.0 (4)	O42—C41—C42—O44	10.4 (4)
O31—C31—C32—O34	179.0 (3)	O41—C41—C42—O44	−170.9 (3)

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O11—H11 $\cdots$ O43	0.82	1.82	2.593 (4)	157
O21—H21 $\cdots$ O33 <sup>i</sup>	0.82	1.79	2.600 (4)	169
O31—H31 $\cdots$ O34 <sup>ii</sup>	0.82	1.76	2.578 (3)	173
O41—H41 $\cdots$ O44 <sup>iii</sup>	0.82	1.80	2.616 (3)	177
N11—H11A $\cdots$ O44 <sup>iv</sup>	0.89	2.02	2.820 (4)	150
N11—H11B $\cdots$ O33 <sup>i</sup>	0.89	1.97	2.856 (4)	178
N11—H11C $\cdots$ O22 <sup>iii</sup>	0.89	2.04	2.898 (4)	162
N21—H21A $\cdots$ O32 <sup>ii</sup>	0.89	2.20	3.013 (4)	152
N21—H21B $\cdots$ O12 <sup>ii</sup>	0.89	1.97	2.795 (4)	154
N21—H21C $\cdots$ O43	0.89	2.07	2.902 (4)	155

Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $1 + x, y, z$ ; (iii)  $x - 1, y, z$ ; (iv)  $x - 1, y - 1, z$ .

All the H atoms were positioned geometrically and were allowed to ride on their respective carrier atoms, with C—H = 0.96 Å, N—H = 0.89 Å, O—H = 0.82 Å and  $U_{iso} = 0.05 \text{ \AA}^2$ . Friedel pairs were merged before the final cycles of refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989; cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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