DL-Alaninium semi-oxalate monohydrate

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The structure of the title compound, $C_3H_8NO_2{}^+ \cdot C_2HO_4{}^- \cdot H_2O$, is formed by two chiral counterparts (L- and D-alaninium cations), semi-oxalate anions and water molecules, with a 1:1:1 cation–anion–water ratio. The structure is compared with that of the previously known anhydrous DL-alaninium semi-oxalate [Subha Nandhini, Krishnakumar & Natarajan (2001). *Acta Cryst.* E**57**, o666–o668] in order to investigate the role of water molecules in the crystal packing. The structure of the hydrate resembles that of anhydrous alaninium semi-oxalate, with the water molecule incorporated into the general three-dimensional network of hydrogen bonds where it forms four hydrogen bonds with neighbours disposed tetrahedrally about it. Although the main structural motifs in the hydrate and in the anhydrous form are topologically similar, the incorporation of water molecules in the network results in significant geometric distortion. There are several types of hydrogen bond in the crystal structure of the hydrate, two of which (O—H···O bonds between the semi-oxalate anions and O—H···O hydrogen bonds between water and alaninium cations) are very short. Such hydrogen bonds between semi-oxalate anions are also present in the anhydrous form of this compound. Short distances between semi-oxalate anions in neighbouring chains in the hydrate alternate with longer ones, whereas in the anhydrous structure they are equidistant. Despite the similarity of these compounds, dehydration of the hydrate on storage is not of a single-crystal to single-crystal type, but gives a polycrystalline pseudomorph, preserving the crystal habit. This transformation proceeds through the formation of an intermediate compound, presumably a hemihydrate.

Comment

Amino acids and their salts attract attention as drugs, biomimetics and molecular materials (Boldyreva, 2007). They are interesting for crystal engineering as individual components and together with other compounds, such as carboxylic acids. The amino and carboxyl groups, and in many cases also the

side chains, of amino acids are capable of forming hydrogen bonds, giving rise to a variety of crystal structures. Of special interest is the comparison of the crystal structures of amino acids and their salts with those of the corresponding solvates, to determine whether the solvate molecules can compete for the formation of hydrogen bonds with the amino or carboxyl groups of the amino acid molecules. Even for the simplest amino and dicarboxylic acids (glycine and oxalic acid), several crystal structures with different stoichiometries of the anhydrous forms, as well as a methanol solvate, have been reported (Chitra & Choudhury, 2007; Chitra *et al.*, 2006; Tumanov *et al.*, 2010). Alanine is the smallest and simplest chiral amino acid. The crystal structures of the salts formed by alanine and oxalic acid have been described, namely DL-alaninium semi-oxalate (Subha Nandhini *et al.*, 2001a) and L-alaninium semi-oxalate (Subha Nandhini *et al.*, 2001b). The present contribution reports the structure of a new member of the same family, the title monohydrate of DL-alaninium semi-oxalate, (I).

(I)
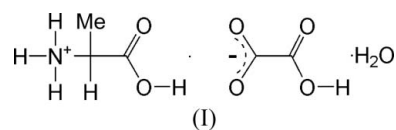
The asymmetric unit of the centrosymmetric crystal structure of (I) contains one alaninium cation, one semi-oxalate anion and one molecule of water (Fig. 1). The crystal structure of the hydrate resembles that of anhydrous alaninium semi-oxalate, with water molecules incorporated into the general three-dimensional hydrogen-bond network: each water molecule forms four hydrogen bonds with neighbours disposed tetrahedrally about it (Fig. 2). The semi-oxalate anion in (I) is not fully flat, whereas the same torsion angle in the anhydrous form (O6—C4—C5—O3) is closer to 180° (Table 1). The torsion angles in the alaninium cations, *viz.* O1—C1—C2—N1 and O1—C1—C2—C3, are also different in the hydrate and in the anhydrous form. These intramolecular changes are a response to the distortion of the intermolecular hydrogen-bond network.

The main structure-forming motif in the crystal structures of individual amino acids is a head-to-tail chain, in which amino
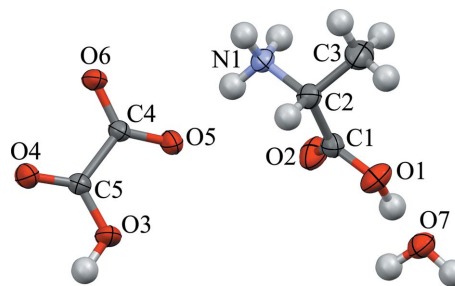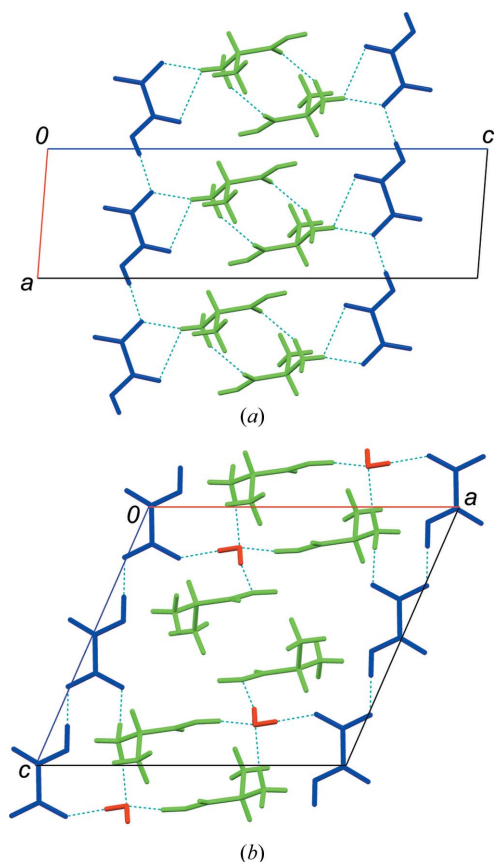

Figure 1
The asymmetric unit of DL-alaninium semi-oxalate hydrate, (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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(a)

(b)

Figure 2
Fragments of the crystal structures of (a) anhydrous DL-alaninium semi-oxalate (Subha Nandhini *et al.*, 2001a) and (b) DL-alaninium semi-oxalate hydrate, (I), viewed along the [010] direction. Hydrogen bonds are shown as dashed lines.

groups are linked to carboxyl groups (Boldyreva, 2007; Görbitz, 2010). It is in these chains that proton transfer results in the formation of zwitterions, *i.e.* NH_3^+–CH(R)–COO$^-$, instead of less polar NH_2–CH(R)–COOH molecules. In the salts of amino acids, these motifs are often not observed.

A structural motif that seems to be common for oxalates of amino acids is a chain formed by the semi-oxalate anions. This motif, $C(5)$ according to the classification suggested by Bernstein (2002), is also present in the crystal structures of alaninium semi-oxalate and its hydrate (Fig. 3). Although the chains in the hydrate and in the anhydrous forms are topologically similar, incorporation of water molecules into the network, linking the chains with each other, results in significant geometric distortion. In the anhydrous form, all neighbouring semi-oxalate anions in the chains are practically in the same plane, whereas in the hydrate the angle between two neighbouring semi-oxalate anions in the chain is close to 30°.

In the hydrate, the O···O distances in the O—H···O hydrogen bonds linking anions along the [001] direction are shorter than the corresponding distances in the anhydrous form (respective O3···O6 distances in Tables 2 and 3). Another difference between the anhydrous form and the hydrate is related to the shortest C···C distances between the semi-oxalate anions in neighbouring chains: in the anhydrous
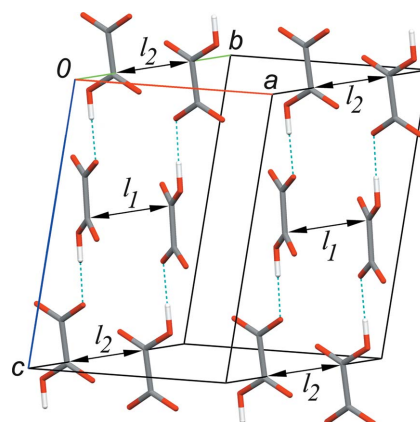
Figure 3
Chains of semi-oxalate anions in the crystal structure of (I). Hydrogen bonds are shown as dashed lines. The distances l_1 and l_2 between C atoms of anions in neighbouring chains are shown by black double-headed arrows. Alaninium anions and water molecules have been omitted for clarity.

form, all these distances l are 3.719 (3) Å at 293 K, whereas in the hydrate, the C···C distances between the semi-oxalate chains are usual for this class of compounds [l_1 = 3.435 (2) Å at 300 K] and alternate with shorter contacts [l_2 = 3.186 (2) Å at 300 K] (Fig. 3). To the best of our knowledge, such short contacts between semi-oxalate chains have not been reported before, and they must arise because of the way the chains are

(a)

(b)
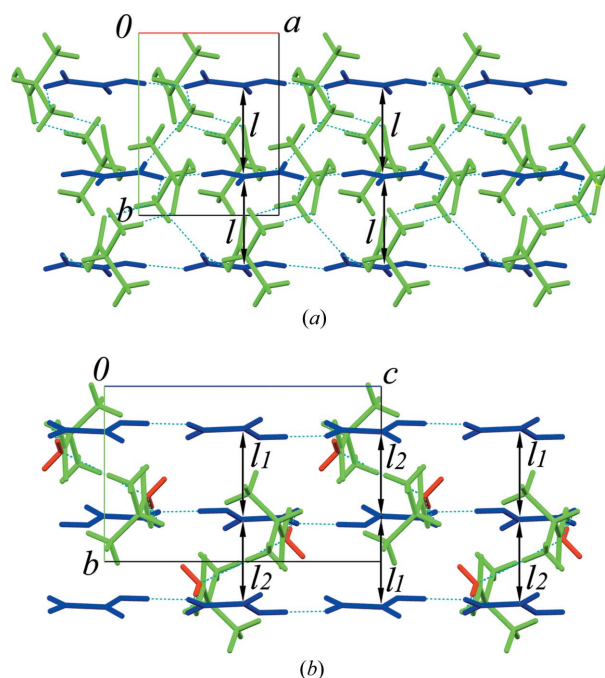
Figure 4
Hydrogen bonds (shown as dashed lines) linking chains of semi-oxalate anions (a) *via* alaninium cations only, in the crystal structure of anhydrous DL-alaninium semi-oxalate, or (b) *via* alaninium cations and water molecules, in the crystal structure of DL-alaninium semi-oxalate hydrate, (I) (viewed along the [001] and [100] directions, respectively). The distances l, l_1 and l_2 between C atoms of anions in neighbouring chains are shown by black double-headed arrows. Dangling bonds have been omitted for clarity.

linked to each other *via* alaninium cations and water molecules (Fig. 4). A similar effect, although with alternating normal and unusually long C···C distances, has been observed previously in DL-lysinium hydrogen oxalate dihydrate (Venkatraman *et al.*, 1997), where semi-oxalate chains are linked alternately by water and lysine molecules, resulting in C···C contact distances of 3.713 (5) Å (reasonably normal for this class of compounds) between semi-oxalate chains in the structure, alternating with very long distances of 7.092 (5) Å.

The semi-oxalate chains in the structure of the hydrate are linked to each other in the [010] direction *via* bridges between water molecules and alaninium cations, forming an $R_6^6(16)$ ring motif. They are further connected to each other in the [120] and [210] directions *via* a cluster of two water molecules and two alaninium cations to give an $R_2^4(14)$ motif, thereby completing the three-dimensional network (Fig. 5). The $R_6^6(16)$ motif is formed by weak N—H···O and O—H···O hydrogen bonds, where the ammonium group of the alaninium cation is connected to the water molecule and the semi-oxalate anion (N1···O7^{ii} and N1···O6^i hydrogen bonds, respectively; symmetry codes as in Table 2), and the water molecule is linked to another semi-oxalate anion by another hydrogen bond (O7···O5^{iii}). In the $R_2^4(14)$ ring, the same hydrogen-bond parameters are observed, but the water molecule is hydrogen bonded with the carboxyl group of the alaninium cation instead of with the semi-oxalate anion, resulting in a strong O1···O7 hydrogen bond (Table 2).

A comparison of the hydrate structure with that of the anhydrous form reveals that, in the anhydrous form, the semi-oxalate chains are linked to each other in the [011] direction *via* rings formed by two alaninium cations, which are very similar to those present in the hydrate (Fig. 2). In the structure of the anhydrous form, the semi-oxalate chains are linked to each other *via* alaninium dimers in the [010] direction, forming weak N1—H···O6 and strong O1—H···O5^i hydrogen bonds with the deprotonated O atoms of the carboxylate groups (Table 3 and Fig. 2). The water molecule embedded in the structure of the hydrate finds the most favourable position to form strong hydrogen bonds: the O1···O7 distance between the water O atom and the carboxyl group of the alaninium cation is 2.6234 (14) Å at 300 K. The water molecule also occupies the most suitable position to achieve tetrahedral coordination *via* four hydrogen bonds to three alaninium cations and one semi-oxalate anion, while, remarkably, the main structural framework of the anhydrous form is to a large extent preserved.

A comparison of the proton-donating and proton-accepting groups in the hydrogen-bond network shows the following details. In the anhydrous form, the alaninium cations are linked to each other *via* N—H···O hydrogen bonds; the amino group of a cation receives an H atom from the oxalic acid. In the hydrate, there are no hydrogen bonds directly linking the alaninium cations with each other, but rather they are connected *via* water molecules or, in an even more complicated way, *via* water and semi-oxalate bridges (Fig. 5). A water molecule acts as a hydrogen-bond donor to a carboxyl group of one alaninium cation, but at the same time also acts
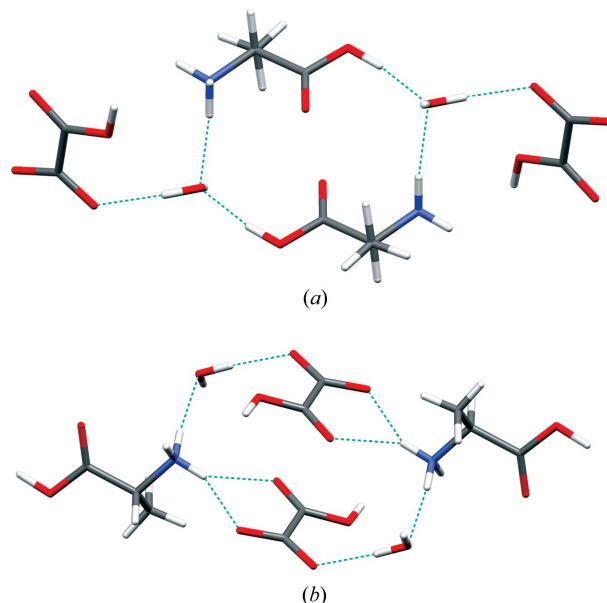

Figure 5
(*a*) $R_2^4(14)$ and (*b*) $R_6^6(16)$ ring motifs in the crystal structure of DL-alaninium semi-oxalate hydrate, (I). Hydrogen bonds are shown as dashed lines.

as a hydrogen-bond acceptor for the carboxyl and ammonium groups of other neighbouring alaninium cations. It also acts as a hydrogen-bond donor in the O—H···O hydrogen bond to a carboxylate group of a neighbouring semi-oxalate anion (Fig. 2).

The inclusion of water molecules into the structural framework of (I) also has a noticeable effect on the weak N—H···O hydrogen bonds. Thus, the N—H···O interactions between alaninium cations and semi-oxalate anions (N1···O5 and N1···O6^i, respectively) are somewhat shorter than those in the anhydrous form, while the N1···O7^{ii} bonds formed by the water molecules are weak (symmetry codes as in Tables 2 and 3).

When stored in air, (I) transforms into DL-alaninium semi-oxalate within 8–12 h at room temperature, as has been confirmed by X-ray powder diffraction analysis. Despite the similarity of the two structures, the dehydration of the hydrate on storage is not of a single-crystal to single-crystal type, but gives a polycrystalline pseudomorph, preserving the crystal habit. This transformation proceeds through the formation of an intermediate compound, presumably a hemihydrate, as has been shown by thermogravimetric analysis. Unfortunately, we could not collect either single-crystal or powder X-ray diffraction data, and could not measure vibrational spectra of this intermediate compound, because of its low stability.

It is interesting to compare the structures of DL-alaninium semi-oxalate and its hydrate with the third structure from the same family, namely L-alaninium semi-oxalate. This compound crystallizes in the space group $P2_12_12_1$, *i.e.* in another crystal system. The chains of the semi-oxalate anions are also present in the structure of L-alaninium semi-oxalate. The O3···O6 distance in the O3—H···O6($1 + x, y, z$) bond is 2.545 (2) Å at 293 K. In both the hydrate and anhydrous forms of DL-alani-

nium semi-oxalate, the corresponding distances are somewhat longer, but these chains are linked to each other by bridges consisting of only one alaninum cation, and no ring motifs are found. This difference in the crystal packing also affects the N—H⋯O hydrogen bonds between L-alaninium cations and semi-oxalate anions in the chains: at 293 K in L-alaninium semi-oxalate the N⋯O distances in these bonds are 2.728 (2) [N1⋯O6($-x, \frac{1}{2} + y, \frac{1}{2} - z$)] and 2.896 (2) Å (N1⋯O5). Thus, for L-alaninium semi-oxalate, the lengths of the N—H⋯O hydrogen bonds are not equal, whereas in the DL-alaninium semi-oxalates they are.

Finally, one can compare the crystal structures of the L- and DL-alaninium semi-oxalates (both hydrate and anhydrous forms) with those of glycinium semi-oxalate and its methanol solvate (Tumanov et al., 2010). Increasing the size of the amino acid by introducing a bulky –CH$_3$ group has an effect on the way the dimers of the amino acid cations link the semi-oxalate chains in the crystal structure, as well as on the structure of the semi-oxalate chains themselves and their mutual orientation. In the structure of the glycinium semi-oxalate, individual amino acid molecules link the semi-oxalate chains to one another, while the glycinium cation dimers link stacks of semi-oxalate chains. Such semi-oxalate chains are not found in the structure of the methanol solvate of bis-glycinium oxalate. In the glycinium semi-oxalate, the oxalate chains are undulating, while they are flat in both the anhydrous DL-alaninium semi-oxalate and the L-alaninium semi-oxalate structures. In the hydrated form of DL-alaninium semi-oxalate, neighbouring semi-oxalate chains lie in different planes. The incorporation of solvent molecules into the crystal structures of DL-alaninium semi-oxalate hydrate and the methanol solvate of bis-glycinium oxalate is similar: the main structural framework is preserved, but the solvent molecules act as bridges between amino acid cations, thus preventing the cations from forming hydrogen bonds with one another. It appears that the coordination shell of a solvated amino acid cation existing in solution is partly preserved in the crystal structure.

Experimental

Crystals of DL-alaninium semi-oxalate hydrate, (I), were obtained by slow cooling of an aqueous solution of DL-alanine and oxalic acid in a 1:1 stoichiometric ratio saturated at 323 K. To avoid decomposition during the diffraction experiment, the sample was protected with cryo-oil.

Crystal data

C$_3$H$_8$NO$_2$$^+$·C$_2HO_4$$^-$·H$_2$O
M_r = 197.15
Monoclinic, $P2_1/c$
a = 12.4987 (19) Å
b = 6.6017 (6) Å
c = 11.3732 (18) Å
β = 113.585 (12)°

V = 860.0 (2) Å^3
Z = 4
Mo Kα radiation
μ = 0.15 mm^{-1}
T = 300 K
0.40 × 0.30 × 0.15 mm

Data collection

Stoe IPDS II diffractometer
7933 measured reflections
2303 independent reflections

1771 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Table 1
Torsion angles (°) for hydrated and anhydrous forms of DL-alaninium semi-oxalate.

	Hydrated form[a]	Anhydrous form[b]
O4—C5—C4—O5	175.78 (12)	176.9 (3)
O3—C5—C4—O5	−4.11 (17)	−4.0 (3)
O4—C5—C4—O6	−5.08 (18)	−2.1 (4)
O3—C5—C4—O6	175.03 (11)	177.1 (2)
O2—C1—C2—N1	2.64 (17)	6.2 (3)
O1—C1—C2—N1	−177.80 (10)	174.0 (2)
O2—C1—C2—C3	125.29 (15)	129.1 (3)
O1—C1—C2—C3	−55.14 (15)	−51.0 (3)

References: (a) this work [for convenience of the comparison, the torsion angles of the inverted cation and anion, which are also present in the unit cell of (I), have been used]; (b) Subha Nandhini et al. (2001a).

Table 2
Hydrogen-bond geometry for (I) (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1C⋯O6^i	0.89	1.99	2.7794 (14)	147
N1—H1C⋯O4^i	0.89	2.36	3.0616 (13)	136
N1—H1B⋯O7^{ii}	0.89	2.02	2.9034 (15)	169
N1—H1A⋯O5	0.89	1.91	2.7893 (14)	168
O7—H7A⋯O5^{iii}	0.89 (2)	1.84 (2)	2.7257 (14)	175.7 (19)
O7—H7B⋯O1^{iv}	0.89 (3)	2.02 (3)	2.8976 (16)	167 (2)
O3—H3⋯O6^v	1.00 (3)	1.57 (3)	2.5732 (13)	178 (3)
O1—H1⋯O7	0.82	1.81	2.6234 (14)	171

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

Table 3
Hydrogen-bond geometry for DL-alaninium semi-oxalate (Å, °).

Data from Subha Nandhini et al. (2001a).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O5^i	0.82	1.80	2.591 (2)	160.6
O3—H1A⋯O6^{ii}	0.82	1.77	2.587 (2)	174.0
N1—H1A⋯O5^{iii}	0.89	1.98	2.834 (3)	161.1
N1—H1B⋯O2^{iv}	0.89	2.03	2.863 (3)	154.2
N1—H1C⋯O6	0.89	1.96	2.818 (2)	162.0

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

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.104
S = 1.04
2303 reflections
145 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

All H atoms were initially located in a difference Fourier map. The positions of the water, oxalate and cation methine H atoms were refined isotropically. The positions of all other H atoms were subsequently geometrically optimized and refined using a riding model, with C—H = 0.96 Å, N—H = 0.89 Å and O—H = 0.82 Å. The tetrahedral methyl and ammonium groups were allowed to rotate, but not to tip. The isotropic displacement parameters of all H atoms were refined freely.

Data collection: X-AREA (Stoe & Cie, 2006); cell refinement: X-AREA; data reduction: X-RED (Stoe & Cie, 2006); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and

X-STEP32 (Stoe & Cie, 2000); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *Mercury*, *PLATON* (Spek, 2009), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3041). Services for accessing these data are described at the back of the journal.

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