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Bis(DL-cysteinium) oxalate

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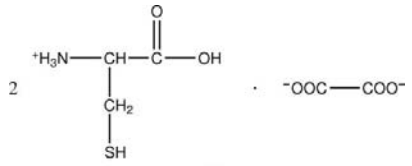
In the title compound, $2C_3H_8NO_2S^+\cdot C_2O_4^{2-}$, the oxalate anion occupies an inversion centre and is coordinated to cysteine molecules of different chirality (L and D) *via* O—H···O and N—H···O hydrogen bonds, the resulting cysteine–oxalate stoichiometry in the crystal structure being 2:1. The oxalate anion is completely deprotonated, whereas cysteine has a positively charged $-NH_3^+$ group and a neutral protonated carboxyl group. The structure is built from infinite hydrogen-bonded triple layers, consisting of an oxalate layer in the middle with layers of L- and D-cysteine molecules on either side. The thiol groups are at the external sides of the layers and form S—H···O hydrogen bonds with the carboxyl groups of neighbouring cysteine molecules. An interesting feature of the structure is the occurrence of short S···S contacts between SH groups of molecules in neighbouring layers, which form not S—H···S but S—H···O intermolecular hydrogen bonds. Due to the effects of crystal packing and intermolecular hydrogen-bond formation, the conformation of the cysteine cation in the title structure is different from that calculated theoretically for an individual cation, as well as from those of cysteine zwitterions in crystals of pure cysteine.

Comment

Amino acids cocrystallize easily with organic acids in general and with oxalic acid in particular. These systems are interesting as molecular materials; for example, many of them exhibit nonlinear optical properties. A comparative study of the conformations of the molecules, the packing motifs and the hydrogen-bond networks in crystals of pure amino acids and in their cocrystals with organic acids is interesting for crystal engineering and for understanding structure–property relationships. The systems can also serve as biomimetics, providing information on the interrelation between conformation and environment for the molecular fragments from which biopolymers are built. The Cambridge Structural Database (CSD, Version 5.29 of January 2008; Allen, 2002) has 18 entries for oxalates of amino acids with the hemi-oxalate ion and with the oxalate ion. The oxalate ion can occupy an inversion centre, as, for example, in the structures of bis(DL-aspartic acid) oxalate (Alagar *et al.*, 2003), bis(glycinium) oxalate (Chitra *et al.*, 2006) and bis(DL-serinium) oxalate dihydrate (Alagar *et al.*, 2002). Such structures have an amino acid–oxalate stoichiometry of 2:1. They can be formed either by nonchiral (glycine) or by racemic amino acids, having an equal number of L- and D-molecules in the crystal structure. In addition to the previously known examples, we describe here a new crystal structure, that of bis(DL-cysteinium) oxalate, (I). In this structure, the oxalate anion occupies an inversion centre and is coordinated to cysteine molecules of different chirality (L and D) *via* O—H···O and N—H···O hydrogen bonds, the resulting stoichiometry of cysteine to oxalate in the crystal structure being 2:1. The asymmetric unit of the structure is shown in Fig. 1.



(I)

The oxalate anion is flat and completely deprotonated, whereas cysteine has a positively charged $-NH_3^+$ group and a neutral protonated carboxyl group, so that the cocrystal is an oxalic acid salt of cysteine. Three H atoms remain localized at the N atom, so that the NH_3 'tail' is positively charged, and cysteine can be considered as a cation. The C1—O1 and C1—O2 distances and O1—C1—C2 and O2—C1—C2 angles differ noticeably (Table 1). The conformation of the cysteine cation in (I) (see torsion angles in Table 1) is different both from those of the cysteine zwitterions (carboxyl group deprotonated) in the crystal structures of pure cysteine in both monoclinic (Harding & Long, 1968; Görbitz & Dalhus, 1996) and orthorhombic L-cysteine (Kerr & Ashmore, 1973; Kerr *et al.*, 1975; Moggach *et al.*, 2005) or in DL-cysteine (Luger & Weber, 1999), and from the conformation of neutral cysteine molecules (with neutral NH_2 'tails') (Dobrowolski *et al.*, 2007).

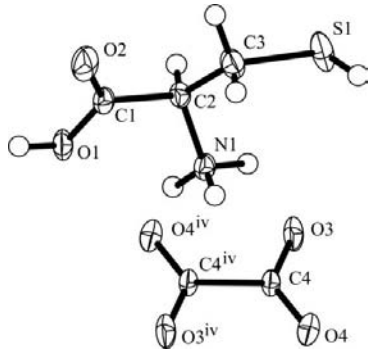


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (iv) $-x+2$, $-y+1$, $-z$.]

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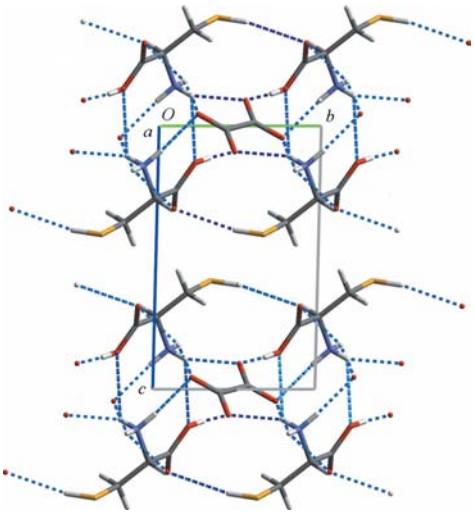

Figure 2
A fragment of the crystal structure of (I), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

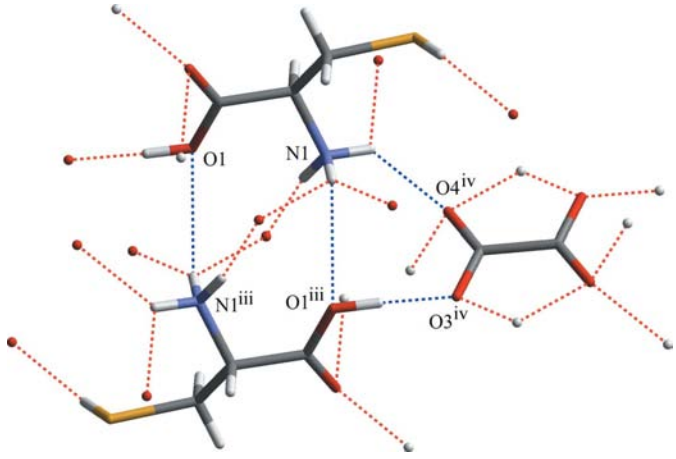

Figure 3
Cations of L- and D-cysteine, related by an inversion centre. Hydrogen bonds linking the cysteine dimer to the oxalate anion are shown as dashed lines. [Symmetry codes: (iii) $-x+2, -y+2, -z$; (iv) $-x+2, -y+1, -z$.]

The cysteine molecules/zwitterions/cations are flexible and can easily change their conformation *via* a rotation around the C1—C2 and C2—C3 bonds. For neutral isolated molecules, the optimum conformation is determined by the possibility of forming intramolecular hydrogen bonds in which the carboxyl, amino and thiol groups are involved (Dobrowolski *et al.*, 2007). In the crystal structures, instead of forming intramolecular hydrogen bonds, cysteine zwitterions (in pure cysteine) or cations (in cysteine salts) form intermolecular hydrogen bonds, the different conformations corresponding to different types of hydrogen bonding.

In the structure of (I), hydrogen bonds link cysteine cations with oxalate anions, and cysteine cations with each other (Table 2, and Figs. 2 and 3). The structure is built from infinite hydrogen-bonded triple layers, consisting of an oxalate layer in the middle with layers of L- and D-cysteine molecules on either side (Fig. 2). The thiol groups are at the external sides of the layers. They are ordered and form S—H···O hydrogen bonds with the carboxyl groups of neighbouring cysteine molecules. Weak S1—H1s···O2^{vi} hydrogen bonds [symmetry code: (vi) $x+1, y-1, z$] link the cysteine cations into infinite chains along the [110] direction. For comparison, in the crystal structure of pure cysteine, the S—H···O contacts are not the dominant ones: the thiol groups can be disordered over S—H···S and S—H···O contacts, as in orthorhombic L-cysteine, or one of the crystallographically independent zwitterions can form S—H···O contacts and another S—H···S contacts, as in monoclinic L-cysteine, or the thiol groups can be ordered and form S—H···S hydrogen bonds exclusively, as in DL-cysteine and in orthorhombic L-cysteine at low temperatures. Interestingly enough, the S···O distance in the hydrogen bonds in (I) [3.6200 (15) Å] is longer than the corresponding distances in the contacts, which are not hydrogen bonds, in the crystal structures of pure cysteine [3.479 Å in orthorhombic L-cysteine at 30 K (Moggach *et al.*, 2005), 3.404 Å in monoclinic cysteine (Görbitz & Dalhus, 1996) and 3.084 Å in DL-cysteine (Luger & Weber, 1999)].

Each oxalate anion of (I) is linked *via* N—H···O and O—H···O hydrogen bonds to eight cysteine cations (four L- and four D-isomers). In turn, each cysteine cation forms hydrogen bonds with four oxalate anions, four cations of the same chirality and a cysteine cation of the opposite chirality. A centrosymmetric dimer is formed by an L- and a D-cation linked by a long N1—H1n···O1^{iii} hydrogen bond [symmetry code: (iii) $-x+2, -y+2, -z$] (Table 2 and Fig. 3). The geometric parameters characterizing this bond are quite comparable with those typically observed for three-centred/bifurcated or four-centred hydrogen bonds (Jeffrey, 1997). The shortest hydrogen bond, *viz.* O1—H1o···O3^{v} [symmetry code: (v) $x-1, y+1, z$], links an oxalate anion with the COOH group of the cysteine cation (Table 2 and Fig. 3). According to its geometric parameters, this hydrogen bond can be classified as an intermediate between a strong and a medium hydrogen bond (Jeffrey, 1997).

Another interesting feature of the structure of (I) is the presence of short S···S contacts [3.5176 (8) Å] between molecules in neighbouring layers. The H atom of the thiol group is involved in the formation of S—H···O bonds with the carboxyl group, so that no short S—H···S hydrogen bonds are formed. Such short S···S contacts are not observed in the structures of pure cysteine, the S···S distances being 3.851 Å between neighbouring molecules in orthorhombic L-cysteine (Kerr *et al.*, 1975), 3.589 and 4.080 Å in monoclinic L-cysteine (Görbitz & Dalhus, 1996) and 3.855 Å in DL-cysteine (Luger & Weber, 1999). In the CSD, only seven structures could be retrieved having shorter S···S contacts between the SH groups than the S···S contact in the structure of (I). Six of these structures are *n*-alkylthiols (Thalladi *et al.*, 2000) and are all built up of long-chain molecules with a variable number *n* of the methylene groups in the chain, $(CH_2)_n$, the thiol groups being located at the two ends of these molecules. The seventh structure is monoclinic L-cysteine (Görbitz & Dalhus, 1996).

Two short C—H···O contacts can be found in the structure of (I) (Table 2). The longer contact is between layers while the shorter links neighbouring molecules within a layer.

According to our unpublished observations, bis(DL-cysteinium) oxalate is more stable with respect to oxidation and the formation of the S—S covalent bond than is pure cysteine, despite the presence of the short S···S contact in the crystal structure of the salt. This may be due to proton transfer from oxalic acid to cysteine during salt formation. At the same time, it can be noted that the crystal structure of DL-homocysteine monohydrate oxalate has been described (Bigoli *et al.*, 1981), in which one of the two crystallographically independent cysteine molecules has a charged deprotonated carboxylate group (COO^-) and the other a neutral protonated carboxyl group (COOH), linked to a hemioxalate ion *via* an O—H···O hydrogen bond.

Experimental

DL-Cysteine (252 mg, 2.1 mmol) and oxalic acid dihydrate (252 mg, 2.0 mmol) were dissolved in distilled water (4.5 ml). Crystals of (I) were grown by slow addition of propan-2-ol (5.5 ml) at 283 K. Solutions containing cysteine and oxalic acid were stable for an indefinite period with respect to oxidation in air, in contrast with solutions of pure cysteine.

Crystal data

$2C_3H_8NO_2S^+\cdot C_2O_4^{2-}$
M_r = 332.34
Triclinic, $P\overline{1}$
a = 5.2779 (6) Å
b = 6.6526 (7) Å
c = 10.4424 (15) Å
α = 86.840 (11)°
β = 76.844 (11)°
γ = 70.097 (10)°
V = 335.60 (8) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 295 (2) K
0.31 × 0.20 × 0.14 mm

Data collection

Stoe Stadi-4 four-circle D094 diffractometer
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1997)
T_{min} = 0.833, T_{max} = 0.939
6198 measured reflections
2946 independent reflections
2215 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
3 standard reflections
frequency: 180 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.117
S = 1.08
2946 reflections
121 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

All H atoms were found in a difference Fourier map and were refined freely. Subsequently, H atoms bonded to O and S atoms were refined with U_{iso}(H) = 1.5U_{eq}(O) or 1.5U_{eq}(S).

Data collection: *STADI4* (Stoe & Cie, 1997); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-STEP* (Stoe & Cie, 1998) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*, *X-RED* (Stoe & Cie, 1997), *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2008).

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Table 1
Selected geometric parameters (Å, °).

C1—O2	1.2147 (15)	C4—O4	1.2408 (14)
C1—O1	1.2981 (15)	C4—O3	1.2626 (15)
C3—S1	1.8180 (14)		
O2—C1—C2	121.21 (11)	O1—C1—C2	113.29 (10)
O2—C1—C2—N1	145.39 (13)	O1—C1—C2—C3	−160.94 (12)
O1—C1—C2—N1	−37.42 (14)	N1—C2—C3—S1	60.27 (13)
O2—C1—C2—C3	21.87 (18)	C1—C2—C3—S1	−176.64 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2n···O4^{i}	0.89 (2)	2.10 (2)	2.9715 (15)	170 (2)
N1—H3n···O4^{ii}	0.92 (2)	2.29 (2)	3.0106 (14)	135 (2)
N1—H1n···O3	0.85 (2)	2.12 (2)	2.8797 (15)	148 (2)
N1—H1n···O1^{iii}	0.85 (2)	2.61 (2)	3.0726 (16)	115 (2)
N1—H1n···O4^{iv}	0.85 (2)	2.32 (2)	2.9677 (15)	133 (2)
O1—H1o···O3^{v}	0.93 (2)	1.57 (2)	2.4982 (13)	175 (2)
S1—H1s···O2^{vi}	1.135 (19)	2.51 (2)	3.6200 (15)	164 (1)
C2—H2···O2^{vii}	0.976 (17)	2.421 (17)	3.1431 (16)	130 (1)
C3—H32···O2^{viii}	0.99 (2)	2.51 (2)	3.453 (2)	161 (2)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+3, -y+1, -z$; (iii) $-x+2, -y+2, -z$; (iv) $-x+2, -y+1, -z$; (v) $x-1, y+1, z$; (vi) $x+1, y-1, z$; (vii) $x+1, y, z$; (viii) $-x+1, -y+2, -z+1$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3146). Services for accessing these data are described at the back of the journal.

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