

DL-Cysteinium semioxalate

Vasily S. Minkov^a and Elena V. Boldyreva^{a,b*}^aREC-008, Novosibirsk State University, Pirogov str. 2, Novosibirsk 630090, Russian Federation, and ^bInstitute of Solid State Chemistry and Mechanochemistry, SB Russian Academy of Sciences, Kutateladze str. 18, Novosibirsk 630128, Russian Federation

Correspondence e-mail: eboldyreva@yahoo.com

Received 30 January 2009

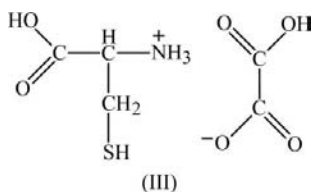
Accepted 9 April 2009

Online 25 April 2009

Two chiral counterparts (L- and D-cysteinium cations related by an inversion centre) are present in the structure of the title compound, $C_3H_8NO_2S^+ \cdot C_2HO_4^-$, with a 1:1 cation–anion ratio. The carboxy group of the cysteinium cation is protonated in the *trans* position relative to the amino group. The crystal structure is built up of double layers, in which dimers of cysteinium cations are connected to each other not directly, but *via* bridges of twisted semioxalate anions linked to each other *via* O–H···O hydrogen bonds forming infinite chains. An interesting feature of the crystal structure is the absence of either S–H···S or S–H···O hydrogen bonds.

Comment

A comparison of the crystals of amino acid salts with those of individual amino acids provides valuable information on the structure–property relationships in these systems, which are widely used as biomimetics, drugs and molecular materials. Cysteine is known for its conformational lability both in pure polymorphs and in salts. The conformational changes involving the $-CH_2SH$ side chains are easily provoked by variations in temperature (Minkov, Chesalov *et al.*, 2008; Minkov *et al.*, 2009; Kolesov *et al.*, 2008) and pressure (Minkov, Krylov *et al.*, 2008), or by changing the crystalline environment in different polymorphs (Harding & Long, 1968; Görbitz & Dalhus, 1996; Minkov *et al.*, 2009) and in different salts (Shan & Huang, 1999; Fujii *et al.*, 2005; Drebushchak *et al.*, 2008; Minkov & Boldyreva, 2008).



Recently, the crystal structures of two salts formed by cysteine and oxalic acid have been described, namely bis-(DL-cysteinium) oxalate (Drebushchak *et al.*, 2008), (I), and L-cysteinium semioxalate (Minkov & Boldyreva, 2008), (II).

The present contribution reports the structure of a new salt from the same family, namely DL-cysteinium semioxalate, (III) (Fig. 1), in which equal amounts of L- and D-cysteinium cations are present, and the total (L + D) cation to semioxalate anion ratio is 1:1.

In (III), the cysteinium cation adopts a *gauche*⁺ conformation (Fig. 1), and the values of the S–C–C–N and S–C–C–C torsion angles are close to those in the low-temperature polymorph of DL-cysteine (Minkov *et al.*, 2009) and in orthorhombic L-cysteine (Kerr & Ashmore, 1973; Kerr *et al.*, 1975), in contrast to the structures of DL-cysteine under ambient conditions (Luger & Weber, 1999), and the structures of (I) (Drebushchak *et al.*, 2008) and (II) (Minkov & Boldyreva, 2008) (Table 1).

The crystal structure of (III) is built up of double layers, in which dimers of cysteinium cations linked by $N1-H1N \cdots O2^{ii}$ hydrogen bonds (Table 2) into a cyclic $R_2^2(10)$ association are connected to each other not directly, but *via* the bridges of slightly twisted [the angle between the two COO planes is $7.1(3)^\circ$] semioxalate anions (Figs. 2 and 3). For comparison, in the structure of (I), L- and D-cysteinium isomers are also linked into dimers *via* N–H···O hydrogen bonds and form similar $R_2^2(10)$ ring motifs, but in (I) the NH group links to a different O atom of the COOH group compared with (III): in

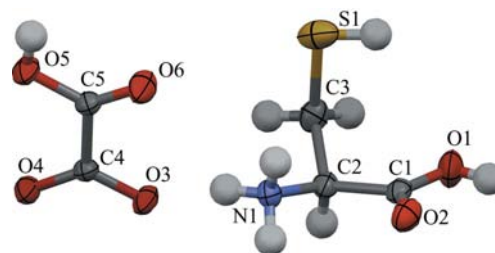


Figure 1

The asymmetric unit of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

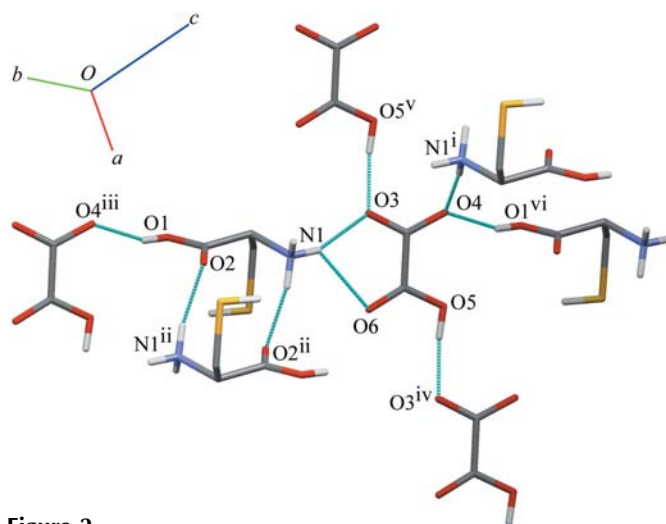


Figure 2

Hydrogen bonding (dashed lines) between the semioxalate anions and cysteinium cations of (III). [Symmetry codes: (v) $-1 + x, y, z$; (vi) $1 + x, y, 1 + z$; for other symmetry codes, see Table 2.] H atoms of CH_2 groups are not shown.

(I) it is the protonated O atom that accepts the second hydrogen, and this results in a longer hydrogen bond [the N—O distance in (I) is 3.0726 (16) Å]. In the structure of (I), the ring is more twisted than in (III), which correlates with a larger twisting [torsion angle N—C—C—O = 37.42 (14)°] of individual molecules in (I) compared with (III). In addition, in (I) there are hydrogen bonds linking the dimers to each other directly. In contrast, in the structure of (II), the cystinium cations are not linked to each other at all. In the present structure, (III), semioxalate anions are linked to each other *via* O5—H5O^{iv}··O3^{iv} hydrogen bonds into infinite C(5) chains along the crystallographic *a* axis (Fig. 2). These chains are also present in the structure of (II), but with shorter O—H··O hydrogen bonds [the O··O distance is 2.5346 (18) Å]. In contrast, in (I) there are no hydrogen bonds between anions. The shortest hydrogen bond in (III) is O1—H1Oⁱⁱⁱ··O4ⁱⁱⁱ in which an oxalate anion accepts a hydrogen bond from the carboxyl group, as is observed in (I). In the crystal structures of (I), (II) and (III), there is a common ring motif of the R₁²(5) type formed by N—H··O bifurcated hydrogen bonds linking the amino group of the cystinium cation and the anion. However, in the structure of (III) this bifurcated bond is more irregular than in (I) and (II) (the difference between the N—O distances in the two N—H··O bonds exceeds 0.2 Å, and that between the O··H distances almost 0.5 Å; see Table 2).

An interesting feature of the crystal structure of (III) is the absence of either S—H··S or S—H··O hydrogen bonds, which is confirmed by the Raman spectrum; only one intense and narrow band of the SH stretching vibrations at 2576 cm⁻¹ is observed, which proves not only that the thiol group forms no hydrogen bonds, but also that the thiol groups in the structure are ordered.

The ability of the molecules of the same chirality in a racemic crystal to form domains (chains and layers) is very interesting and important. For example, serine is prone to forming homochiral clusters even in the gas phase (Yang *et al.*, 2006), and layers of the same chirality can be found in the crystal structure of DL-serine (Kistenmacher *et al.*, 1974). In

contrast, no homochiral chains or layers can be observed in the crystal structures of pure DL-cysteine polymorphs (Minkov *et al.*, 2009). However, the crystallization of cystinium oxalates, unlike pure cysteine, yields homochiral domains. Infinite head-to-tail chains of the cystinium cations linked by oxalate anions are present in (I) (Drebushchak *et al.*, 2008); in (III) the cystinium cations alone do not form any (either homo- or heterochiral) chains, but in each double layer formed by dimers of L- and D-cystinium cations linked *via* semioxalate anions, the L-isomers are all on one side of the double layer, and the D-isomers are on the other (Fig. 3), similar to what has been observed in (I).

Interestingly enough, rapid and slow crystallization from the same solution (see *Experimental*) gives different products: these are, respectively, (I), in which the oxalate anion is completely deprotonated and coordinates the two cystinium isomers from its different sides by the two COO groups, and (III), with a partly deprotonated semioxalate anion and a different coordination type. A similar effect has been reported by Boldyreva & Shikina (2008) for glycinium semioxalate (Subha Nandhini *et al.*, 2001) and bis-glycinium oxalate (Chitra & Choudhury, 2007). This phenomenon may reflect the presence of different types of 'procrystal clusters' in the same solution and the different solubility of the two compounds with a different stoichiometric ratio.

Experimental

Crystals of (III) were obtained by slow evaporation of a saturated aqueous solution of DL-cysteine and oxalic acid in an equimolar ratio. Colourless thick-plate-shaped crystals were obtained.

Crystal data

C ₃ H ₈ NO ₂ S ⁺ ·C ₂ HO ₄ ⁻	γ = 100.119 (3)°
M _r = 211.20	V = 443.62 (4) Å ³
Triclinic, P $\bar{1}$	Z = 2
a = 5.6664 (2) Å	Mo Kα radiation
b = 9.0149 (4) Å	μ = 0.37 mm ⁻¹
c = 9.7749 (5) Å	T = 295 K
α = 109.349 (4)°	0.55 × 0.46 × 0.15 mm
β = 102.282 (3)°	

Data collection

Oxford Diffraction KM-4-CCD diffractometer	13760 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)	2695 independent reflections
T _{min} = 0.814, T _{max} = 0.940	2240 reflections with I > 2σ(I)
	R _{int} = 0.028

Refinement

R[F ² > 2σ(F ²)] = 0.035	H atoms treated by a mixture of independent and constrained refinement
wR(F ²) = 0.101	Δρ _{max} = 0.42 e Å ⁻³
S = 1.09	Δρ _{min} = -0.36 e Å ⁻³
2695 reflections	
151 parameters	

All H atoms were found in a difference Fourier map and were refined freely. Subsequently, methylene H atoms were refined with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: CrysAlis CCD (Oxford Diffraction, 2008); cell refinement: CrysAlis CCD; data reduction: CrysAlis RED (Oxford

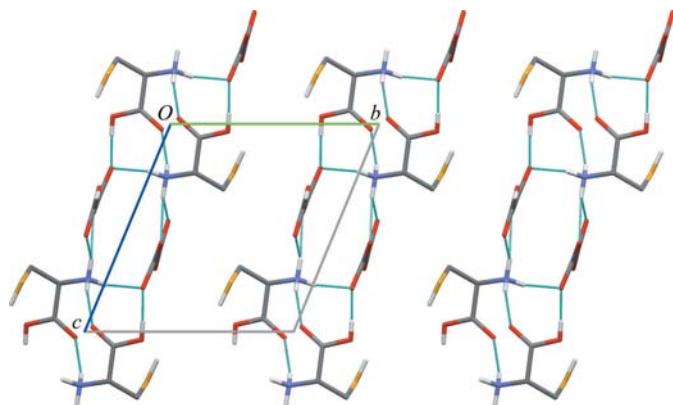


Figure 3

A fragment of the crystal arrangement of (III) projected on the *bc* plane. Hydrogen bonds are shown as dashed lines and H atoms of CH₂ groups are not shown.

Table 1Selected torsion angles ($^{\circ}$).

N1–C2–C1–O2	15.17 (14)	C1–C2–C3–S1	–62.22 (12)
C3–C2–C1–O2	139.43 (12)	O4–C4–C5–O6	171.83 (12)
N1–C2–C1–O1	–166.39 (9)	O3–C4–C5–O6	–6.01 (17)
C3–C2–C1–O1	–42.14 (13)	O4–C4–C5–O5	–6.57 (15)
N1–C2–C3–S1	60.53 (12)	O3–C4–C5–O5	175.59 (10)

Table 2Hydrogen-bond geometry (\AA , $^{\circ}$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H3N \cdots O3	0.860 (18)	1.986 (18)	2.8023 (13)	157.9 (16)
N1–H3N \cdots O6	0.860 (18)	2.484 (17)	3.0694 (14)	126.0 (14)
N1–H2N \cdots O4 ⁱ	0.897 (18)	2.004 (18)	2.8882 (14)	168.4 (15)
N1–H1N \cdots O2 ⁱⁱ	0.870 (18)	2.036 (18)	2.8618 (14)	158.1 (16)
O1–H1O \cdots O4 ⁱⁱⁱ	0.78 (2)	1.82 (2)	2.5682 (12)	159 (2)
O5–H5O \cdots O3 ^{iv}	0.87 (2)	1.74 (2)	2.6076 (12)	172.2 (18)

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

Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2009).

The authors acknowledge financial support from RFBR (grant No. 06-03-90573), the Program of the Presidium of RAS 'Nanomaterials and nanotechnologies' (project 27.44), the Program of the Department of Chemistry and Materials Sciences of the RAS 'Physical chemistry of supramolecular systems' (project 5.6.4.), Integration Project Nos. 13 and 109 of the SB RAS, and a BRHE grant from the CRDF and the Russian Ministry of Science and Education. The diffractometer used for the study was purchased with financial

support from the Innovation Project 'Education' No. 456 from the Russian Ministry of Science and Education.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3159). Services for accessing these data are described at the back of the journal.

References

- Boldyreva, E. V. & Shikina, N. Yu. (2008). INCOME-2008, VIth International Conference on Mechanochemistry and Mechanical Alloying, Jamshedpur, India. Jamshedpur: NML.
- Chitra, R. & Choudhury, R. R. (2007). *Acta Cryst.* **B63**, 497–504.
- Drebushchak, T. N., Bizyaev, S. N. & Boldyreva, E. V. (2008). *Acta Cryst.* **C64**, o313–o315.
- Fujii, I., Baba, H. & Takahashi, Y. (2005). *X-ray Struct. Anal. Online*, **21**, x175–x176.
- Görbitz, C. H. & Dalhus, B. (1996). *Acta Cryst.* **C52**, 1756–1759.
- Harding, M. M. & Long, H. A. (1968). *Acta Cryst.* **B24**, 1096–1102.
- Kerr, K. A. & Ashmore, J. P. (1973). *Acta Cryst.* **B29**, 2124–2127.
- Kerr, K. A., Ashmore, J. P. & Koetzle, T. F. (1975). *Acta Cryst.* **B31**, 2022–2026.
- Kistenmacher, T. J., Rand, G. A. & Marsh, R. E. (1974). *Acta Cryst.* **B30**, 2573–2578.
- Kolesov, B. A., Minkov, V. S., Boldyreva, E. V. & Drebushchak, T. N. (2008). *J. Phys. Chem. B*, **112**, 12827–12839.
- Luger, P. & Weber, M. (1999). *Acta Cryst.* **C55**, 1882–1885.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Minkov, V. S. & Boldyreva, E. V. (2008). *Acta Cryst.* **C64**, o344–o348.
- Minkov, V. S., Chesalov, Yu. A. & Boldyreva, E. V. (2008). *J. Struct. Chem.* **49**, 1062–1074.
- Minkov, V. S., Krylov, A. S., Boldyreva, E. V., Goryainov, S. V., Bizyaev, S. N. & Vtyurin, A. N. (2008). *J. Phys. Chem. B*, **112**, 8851–8854.
- Minkov, V. S., Tumanov, N. A., Kolesov, B. A., Boldyreva, E. V. & Bizyaev, S. N. (2009). *J. Phys. Chem. B*, **113**, 5262–5272.
- Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
- Shan, Y. & Huang, S. D. (1999). *Z. Kristallogr. New Cryst. Struct.* **214**, 41–42.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2001). *Acta Cryst.* **C57**, 115–116.
- Westrip, S. P. (2009). *publCIF*. In preparation.
- Yang, P., Xu, R., Nanita, S. C. & Cooks, R. G. (2006). *J. Am. Chem. Soc.* **128**, 17074–17086.