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Bis(glycinium) oxalate: evidence of strong hydrogen bonding

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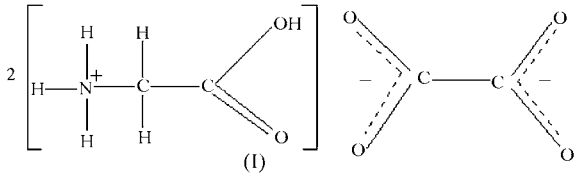
In the title 2:1 salt, $2C_2H_6NO_2^+\cdot C_2O_4^{2-}$, the glycine molecule is in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The doubly charged oxalate anion lies across a crystallographic inversion centre. One of the reasons why the 1:1 glycinium oxalate salt has a higher melting point than the title compound may be the difference in their hydrogen-bonding patterns. A database search for salts formed between amino acids or substituted amino acids and oxalic acid revealed that, in most of the structures, the conformation about the O=C—OH bond is synplanar. D-Tryptophan oxalate is the only example where the OH group of a semi-oxalate adopts an antiplanar conformation. The 2:1 stoichiometry seen in the present salt is observed only in the salts of DL-serine, DL-aspartic acid and betaine with oxalic acid.

Comment

The salts of amino acids with simple carboxylic acids are believed to have existed on the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971). These salts are held together by an extensive network of hydrogen bonds that could provide insight into the principles of biomolecular aggregation and recognition. Amino acid salts exhibit structural phase transitions of various types, and they also exhibit ferroelectric, antiferroelectric or ferroelastic behaviour (Albers, 1988; Schaack, 1990). Glycine is the simplest and the only non-chiral amino acid in nature. It can exist in cationic, zwitterionic or anionic forms. Oxalic acid is the simplest dicarboxylic acid, and it can exist in the oxalate, semi-oxalate or oxalic acid form. A 1:1 salt of glycine and oxalic acid has already been reported (Subha Nandhini *et al.*, 2001*a*), in which glycine exists in the cationic form with a positively charged amine group and an uncharged carboxylic acid group, while oxalic acid exists as the semi-oxalate anion. Salts of oxalic acid with many other natural and substituted amino acids, such as DL-alanine (Subha Nandhini *et al.*, 2001*c*), L-alanine (Subha Nandhini *et al.*, 2001*b*), DL-arginine and L-arginine (Chandra *et al.*, 1998), DL-aspartic acid (Alagar *et al.*, 2003), L-histidine and DL-histidine (Prabu *et al.*, 1996), DL-lysine and L-lysine (Venkatraman *et al.*, 1997), D-tryptophan (Bakke & Mostad, 1980), DL-threonine (Nandhini *et al.*, 2001), L-leucine (Rajagopal *et al.*, 2003), DL-serine (Alagar *et al.*, 2002), β-alaninium (Krishnakumar *et al.*, 2002; Godzisz *et al.*, 2003) and betaine (Rodrigues *et al.*, 2001), have been reported. In these salts, oxalic acid predominantly occurs as the semi-oxalate ion, except in the case of DL-serine, L-lysine and DL-aspartic acid, where one of the species was in the oxalate form.

Using the Cambridge Structural Database (CSD; update 5.26 of November 2004; Allen, 2002), an analysis of the geometry and hydrogen bonding in salts of amino acids or substituted amino acids with oxalic acid has been carried out. Among these salts, a short and very strong O—H···O hydrogen bond involving the carboxyl group of the amino acid has been observed only in the salt with betaine. The O—H···O hydrogen bond in the betaine salt is found between the carboxyl groups of two amino acid molecules; one H atom is shared between two amino acid molecules. The present X-ray study of the of 2:1 glycinium oxalate salt, (I), carried out at room temperature, also reveals a strong and short hydrogen bond involving the amino acid carboxyl group, but in this case the O—H···O bond is between the carboxyl group of the amino acid and the oxalate anion. The other three structures containing an amino acid and the oxalate ion exhibit similar interactions but with longer O···O distances [*i.e.* 2.531 (1) and 2.516 (1) Å for DL-serine, 2.565 (2) Å for DL-aspartic acid, and 2.497 (2) Å for L-lysine, *cf.* 2.454 (1) Å for (I)]. The asymmetric unit consists of half an oxalate ion lying across an inversion centre and one glycinium ion (Fig. 1). The glycine molecule has a positively charged amino group and an uncharged carboxylic acid group, while oxalic acid exists as a doubly charged oxalate anion. Fig. 2 shows the packing of the molecules viewed approximately along the *a* axis. The carboxylate O atoms of the oxalate anion act as hydrogen-bond acceptors. The protonated glycine molecules are linked by N—H···O hydrogen bonds, forming a three dimensional network running along all three principal axes.



(I)

The strengths of O—H···O hydrogen bonds are generally correlated with geometric parameters such as the O—H, H···O and O···O distances and the O—H···O angle (Jeffery, 1997). Very strong hydrogen bonds are observed to have H···O distances of 1.2–1.6 Å, O···O separations of 2.4–2.55 Å and O—H···O angles of 175–180°, with concomitant lengthening of the covalent O—H bond. In the present salt, the carboxyl OH group of glycine makes a very strong hydrogen bond with an O atom of the doubly ionized oxalate ion (Table 1). The two carboxyl groups involved in the strong hydrogen bond also satisfy the essential criterion for the formation of a strong hydrogen bond, namely that the donor

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and acceptor atoms have identical proton affinities in the media in which they co-exist. The long C1—O2 distance [1.2697 (19) Å] in the present structure could be attributed to the presence of a very strong O—H···O hydrogen bond involving this O atom [or the symmetry equivalent atom O2^{i}; symmetry code: (i) $-x, -y+1, -z$]. Apart from these interactions, C—H···O contacts of 2.47 and 2.69 Å have also been observed for both Cα H atoms of glycine.

The 2:1 stoichiometry of amino acid and substituted amino acid oxalates is much more common than other stoichiometries. The 2:1 stoichiometry seen in the present salt is observed in the salts of DL-serine, DL-aspartic acid and betaine with oxalic acid. Interestingly, in DL-serine, DL-aspartic acid and the present structure, the 2:1 stochiometery has been achieved through identical protonation states of the components. The substituted amino acid betaine has a different protonation state (protonated and zwitterionic betaine and semi-oxalate), which could possibly be due to chemical modification of the amino acid.

The conformation of the oxalate or semi-oxalate ion is essentially determined by the torsion angle around the C—O and C—C bonds. In all of the 18 structures found in the CSD, with 22 oxalate or semi-oxalate ions between them, the conformation of the OH group about the O=C—OH bond is synplanar, except in the case of the D-tryptophan salt (Bakke & Mostad, 1980). Although an earlier analysis (Leiserowitz, 1976) found the antiplanar conformation to be associated with an intramolecular hydrogen bond, there is no such intramolecular hydrogen bond in the structure of D-tryptophan oxalate. The distribution of torsion angles around the C—C bond of the oxalic acid molecule was also examined. It was observed that the conformation typically adopted was planar (Chandra *et al.*, 1998). However, in the cases of betanium oxalate and DL-arginine oxalate, these torsion angles are 70.1 (4) and 95.2 (1)°, respectively. In the case of DL-arginine, there are additional hydrogen-bond donors, which form additional hydrogen bonds to the semi-oxalate ions. Twisting of the semi-oxalate ion might therefore reasonably be attributed to the formation of a stable hydrogen-bond network. In the case of betaine, as there is complete methylation of the amine group, there are no hydrogen bonds between the amino acid and oxalate species. The twisting in this case may be due to optimization of electrostatic $O^{-}\cdots N^{+}$ contacts. Hence, these atypical torsion angles cannot be attributed to one factor. The melting points of 2:1 and 1:1 glycinium oxalates were found to be 428 and 449 K, respectively. One of the possible reasons for the higher melting point of glycinium oxalate is the difference in the hydrogen-bonding patterns of the two salts (Table 1).

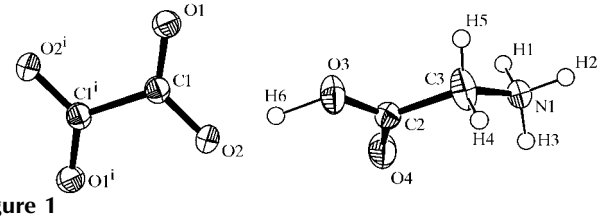

Figure 1
An ellipsoid plot of the title salt, showing the atom-numbering scheme and 50% probability displacement ellipsoids. [Symmetry code: (i) $-x, -y+1, -z$.]

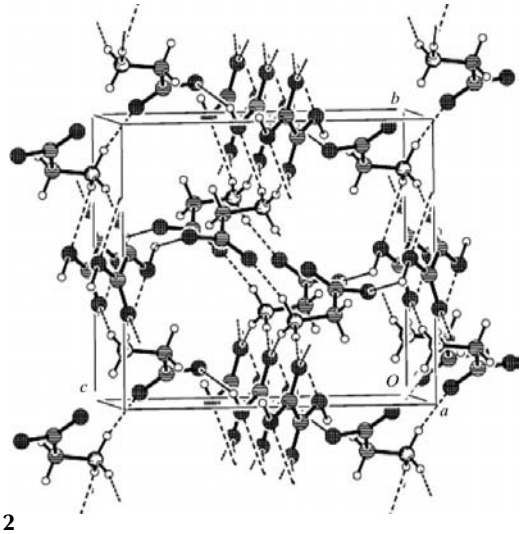

Figure 2
A packing diagram for the title salt, viewed approximately along the *a* axis, showing the three-dimensional hydrogen-bonding network.

Experimental

Colourless single crystals of bis(glycinium) oxalate were grown by slow evaporation from an aqueous solution containing glycine and oxalic acid in a 2:1 molar ratio. The melting points of crystalline samples were determined using differential scanning calorimetry (Mettler Toledeo DSC 821E). The samples were heated at a rate of 10 K min^{-1} from 123 K up to the melting point.

Crystal data

$2C_2H_6NO_2^{+}\cdot C_2O_4^{2-}$	D_x = 1.512 Mg m^{-3}
M_r = 240.16	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 962 reflections
a = 4.9199 (18) Å	θ = 2.8–25.4°
b = 9.959 (4) Å	μ = 0.14 mm^{-1}
c = 10.859 (4) Å	T = 300 K
β = 97.513 (5)°	Irregular, colourless
V = 527.5 (3) Å^3	0.03 × 0.02 × 0.01 mm
Z = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	R_{int} = 0.029
φ and ω scans	θ_{max} = 25.4°
2712 measured reflections	$h = -4 \rightarrow 5$
962 independent reflections	$k = -11 \rightarrow 11$
854 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.1698P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.090	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
962 reflections	Extinction correction: *SHELXL97*
90 parameters	Extinction coefficient: 0.088 (11)
H atoms treated by a mixture of independent and constrained refinement	

All H atoms were found initially in difference Fourier maps. H atoms bonded to atom C3 were placed at geometrically idealized positions (C—H = 0.91 and 0.93 Å) and refined using a riding model, with U_{iso}(H) = 1.5U_{eq}(C). All other H atoms were freely refined.

Table 1
Comparison of hydrogen-bonding geometries (Å, °) in the 2:1 and 1:1 glycinium oxalate salts.

D—H···A	D—H	H···A	D···A	D—H···A
Glycinium oxalate (2:1)				
N1—H1···O1^{ii}	0.93 (2)	2.01 (2)	2.9002 (19)	160.5 (17)
N1—H2···O1^{iii}	0.93 (2)	1.92 (2)	2.8458 (19)	176.7 (17)
N1—H3···O4^{iv}	0.93 (2)	1.96 (2)	2.875 (2)	167.7 (19)
O3—H6···O2	1.11 (3)	1.34 (3)	2.4544 (15)	178 (3)
Glycinium oxalate (1:1)				
N1—H2···O1^{v}	0.94	1.81	2.698	156
N1—H3···O4^{vi}	0.91	2.25	3.082	152
N1—H1···O1^{vii}	0.90	2.26	2.949	133
O3—H6···O2^{viii} of COOH of amino acid	0.86	1.73	2.593	174
O—H···O^{ix} of oxalic acid	0.89	1.65	2.540	177

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1626). Services for accessing these data are described at the back of the journal.

References

Alagar, M., Krishnakumar, R. V., Subha Nandhini, M., Cameron, T. S. & Natarajan, S. (2003). *Acta Cryst.* E**59**, o108–o110.
Alagar, M., Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2002). *Acta Cryst.* E**58**, o114–o116.
Albers, J. (1988). *Ferroelectrics*, **78**, 3–10.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bakke, O. & Mostad, A. (1980). *Acta Chem. Scand. Ser. B*, **34**, 559–570.
Bruker (2004). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chandra, N. R., Prabu, M. M., Venkatraman, J., Suresh, S. & Vijayan, M. (1998). *Acta Cryst.* B**54**, 257–263.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Godzisz, D., Ilczyszyn, M. & Ilczyszyn, M. M. (2003). *Spectrochim. Acta Part A*, **59**, 681–693.
Jeffery, G. A. (1997). In *An Introduction to Hydrogen Bonding*. Oxford University Press.
Krishnakumar, R. V., Subha Nandhini, M. & Natarajan, S. (2002). *Acta Cryst.* E**58**, o117–o119.
Kvenvolden, K. A., Lawless, J. G. & Ponnamperuma, C. (1971). *Proc. Natl Acad. Sci. USA*, **68**, 486–490.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Miller, S. L. & Orgel, E. L. (1974). In *The Origins of Life on the Earth.* New Jersey: Prentice–Hall.
Nandhini, M. S., Krishnakumar, R. V., Malathi, R., Rajan, S. S. & Natarajan, S. (2001). *Acta Cryst.* E**57**, o769–o771.
Prabu, M. M., Nagendra, H. G., Suresh, S. & Vijayan, M. (1996). *J. Biomol. Struct. Dyn.* **14**, 387–392.
Rajagopal, K., Krishnakumar, R. V., Subha Nandhini, M., Malathi, R., Rajan, S. S. & Natarajan, S. (2003). *Acta Cryst.* E**59**, o878–o880.
Rodrigues, V. H., Paixão, J. A., Costa, M. M. R. R. & Matos Beja, A. (2001). *Acta Cryst.* C**57**, 213–215.
Schaack, G. (1990). *Ferroelectrics*, **104**, 147–158.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2001*a*). *Acta Cryst.* C**57**, 115–116.
Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2001*b*). *Acta Cryst.* E**57**, o633–o635.
Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2001*c*). *Acta Cryst.* E**57**, o666–o668.
Venkatraman, J., Prabu, M. M. & Vijayan, M. (1997). *J. Peptide Res.* **50**, 77–87.