Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(glycylglycinium) oxalate at 100 K

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Received 29 July 2003
Accepted 12 August 2003
Online 16 September 2003

The structure of the title compound, $2C_4H_9N_2O_3^+\cdot C_2O_4^{2-}$, which has been determined by X-ray diffraction, contains discrete glycylglycine $(HGly–Gly)^+$ cations in general positions and oxalate anions which lie across centres of inversion. Although the geometry of the $(HGly–Gly)^+$ cation is not significantly different compared with other structures containing this residue, a few changes in conformation are observed which indicate the presence of molecular interactions. The molecular network in the crystal consists of one nearly linear O—H···O, five N—H···O and two weak C—H···O hydrogen bonds.

Comment

Compounds derived from amino acids, often exhibiting weak van der Waals interactions and hydrogen bonds, possess a high degree of delocalization and hence are expected to be more non-linear than their inorganic counterparts. Furthermore, amino acids have peculiar physical and chemical properties which are attributed to the presence of an H-atom-donor carboxylic acid group (–COOH) and an H-atom-acceptor amino group ($–NH_2$). Due to this dipolar nature, amino acids and related compounds often have physical properties which make them potential candidates for non-linear optical (NLO) activity (Fuchs *et al.*, 1989).

The geometry of glycylglycine (Gly–Gly) has been investigated by X-ray and neutron diffraction at room temperature (Biswas *et al.*, 1968; Hughes, 1968; Freeman *et al.*, 1970; Griffin & Coppens, 1975) and at 82 K (Kvick *et al.*, 1977). The X-ray charge densities have been used in the calculation of intermolecular interactions and lattice energies in the crystal of Gly–Gly (Abramov, Volkov & Coppens, 2000; Abramov, Volkov *et al.*, 2000). Analyses of the hydrogen bonds present and their influence on the conformation of the Gly–Gly moiety in the structures of Gly–Gly as the hydrochloride (Parthasarathy, 1969), monohydrochloride monohydrate (Koetzle *et al.*, 1972), nitrate (Narasinga Rao & Parthasarathy, 1973), phosphate monohydrate (Freeman *et al.*, 1972) and phosphite (Averbuch-Pouchot, 1993) have been reported. The interaction between Gly–Gly and polyoxometalates has been examined for an understanding of their antitumour and anti-HIV activity (Crans *et al.*, 1994; Han *et al.*, 2002). We present here the crystal structure of the title salt, (I), obtained from Gly–Gly and oxalic acid.

(I)

The crystals of (I) consist of discrete glycylglycine cations, $(HGly–Gly)^+$, and oxalate dianions, $C_2O_4^{2-}$ (Fig. 1). The characteristic structural features of peptides are the planarity of the peptide group and the constancy of the dimensions of the peptide unit, which are independent of different amino acid constituents. The geometry of the $(HGly–Gly)^+$ cation in (I), as defined by the bond distances and angles, is comparable with the corresponding parameters observed in similar structures containing this residue (Parthasarathy, 1969; Koetzle *et al.*, 1972; Narasinga Rao & Parthasarathy, 1973; Han *et al.*, 2002).

Atoms C2, C3, O4, N5, C6 and H5 define the peptide unit, which is almost planar. The average deviation from the least-squares plane through atoms C2–C6 is 0.01 Å. Furthermore, the planarity of the peptide unit is defined by the torsion angle ω, which characterizes the rotation around the C—N peptide bond. An ω value of 180° corresponds to a planar peptide unit (*trans* conformation). In compound (I), the deviation of ω (C2—C3—N5—C6) from 180° is about 2° (Table 3). The maximum twist around the peptide bond in Gly–Gly structures has been observed in $(HGly–Gly)_3PMo_{12}O_{40}\cdot 4H_2O$ (167.1°; Han *et al.*, 2002); this deviation was attributed to the interaction between the Gly–Gly unit and the polyanion. The full conformation of a peptide chain is described by two additional torsion angles, ψ and φ, which characterize the twist around the C—C^α and N—C^α bonds, respectively. These torsion angles for (I) are given in Table 3 and suggest that the $(HGly–Gly)^+$ cation is in an almost extended conformation. A similar conformation of the $(HGly–Gly)^+$ cation has been reported in Gly–Gly nitrate (Narasinga Rao & Parthasarathy, 1973) and $(HGly–Gly)_3PMo_{12}O_{40}\cdot 4H_2O$ (Han *et al.*, 2002).

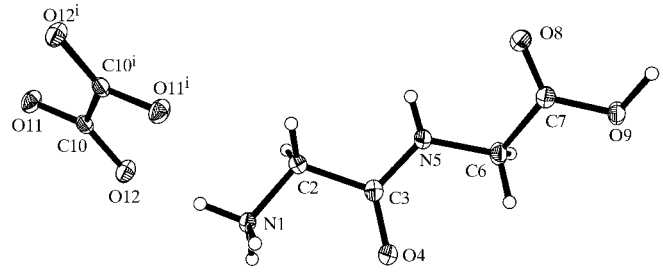

Figure 1
The molecular structure of the $(HGly–Gly)^+$ cation and oxalate dianion in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $2-x, 1-y, 1-z$].

 DOI: 10.1107/S0108270103018031

The carboxylate end of the $(HGly–Gly)^+$ cation of (I) (atoms C6, C7, O8 and O9) is almost planar; the dihedral angle describing the inclination of the carboxylate moiety to the peptide plane (atoms C2, C3, O4, N5 and C6) is 32.57 (6)°. A similar dihedral angle of 32.22 (7)° is observed when the peptide plane is defined only by atoms C2, C3, O4 and N5, as has been performed by Kvick *et al.* (1977). Furthermore, the dihedral angle between the peptide plane and the carboxylate group (atoms C7, O8 and O9) is 31.9 (1)°, which is not significantly different from the values given above. Han *et al.* (2002) calculated this angle by defining the peptide-group plane using only C, N and O atoms in the structure of $(HGly–Gly)_3PMo_{12}O_{40}·4H_2O$, where there are three symmetrically independent $(HGly–Gly)^+$ cations. The dihedral angles in that structure between the plane of the peptide group so defined and the carboxylate group range from 48.3 to 62.6°, which is unusual (Han *et al.*, 2002). By calculating the dihedral angle in this way for (I), using atoms C3/O4/N5 and C7/O8/O9, we obtained a value of 31.6 (2)°. In the present structure, the inclination of the peptide plane to that of the carboxylic acid end or group is greater than 30°, no matter how the peptide or carboxylate (carboxylate end or group) planes are defined. This is in contrast with the principle that the carboxylate and peptide groups are approximately coplanar or perpendicular, as is observed, for example, in glycylglycine nitrate (16.5°; Narasinga Rao & Parthasarathy, 1973) and glycylglycine hydrochloride (77.9°; Parthasarathy, 1969).

The centrosymmetric oxalate dianion in (I) is strictly coplanar. The C10—O11 and C10—O12 bond distances (Table 1) clearly indicate that the carboxylate groups are not protonated. These values and the other geometric parameters correlate well with the corresponding values found in crystal structures containing the $C_2O_4^{2-}$ moiety (Newkome *et al.*, 1985; Van der Brempt *et al.*, 1985; Braga *et al.*, 2002).

The crystal packing in (I) is stabilized by ionic interactions between the $(HGly–Gly)^+$ cations and oxalate dianions, and by strong hydrogen bonds. The N—H···O hydrogen bond involving the peptide N atom is significantly longer than the hydrogen bonds donated by the N atom of the ammonium group, similar to what is observed in the structures of glycylglycine nitrate (Narasinga Rao & Parthasarathy, 1973) and α-glycylglycine (Kvick *et al.*, 1977). The three H atoms of the ammonium group participate in four strong hydrogen bonds. One is to the carboxyl O atom of an $(HGly–Gly)^+$ cation (atom H1*B*) and three involve the oxalate anion (atoms H1*A* and H1*C*; Table 2). Atom H5 of the amide group takes part in only one intercation N—H···O hydrogen bond, involving the amide O atom of a neighbouring cation. Atom H9 of the carboxyl group participates in a nearly linear strong O—H···O hydrogen bond with the O atom of an oxalate anion. Weak C—H···O hydrogen bonds are formed between the H atom of the α C atom (C2) and the O atoms of neighbouring $(HGly–Gly)^+$ cations (Table 2). Overall, the hydrogen bonds link the ions into a three-dimensional framework.

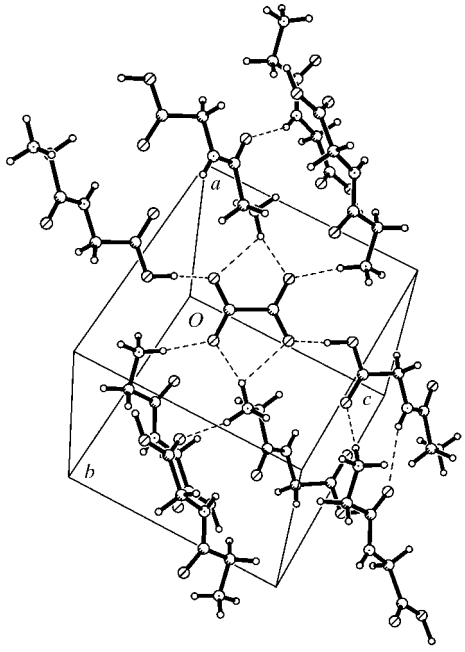

Figure 2
The packing diagram for (I), with hydrogen bonds shown as dashed lines.

Experimental

Crystals of (I) were grown by slow evaporation at room temperature of an aqueous solution containing glycylglycine and oxalic acid in a 1:1 stoichiometric ratio.

Crystal data

$2C_4H_9N_2O_3^+·C_2O_4^{2-}$	D_x = 1.594 Mg m^{-3}
M_r = 354.28	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4592 reflections
a = 8.2384 (7) Å	θ = 3.2–26.3°
b = 10.0582 (9) Å	μ = 0.14 mm^{-1}
c = 8.9323 (8) Å	T = 100.0 (2) K
β = 94.477 (7)°	Cube, colourless
V = 737.90 (11) Å^3	0.20 × 0.18 × 0.16 mm
Z = 2	

Data collection

Oxford Diffraction Xcalibur area-detector diffractometer	R_{int} = 0.031
	θ_{max} = 26.3°
ω scans	$h = -10 \rightarrow 10$
4592 measured reflections	$k = -12 \rightarrow 11$
1495 independent reflections	$l = -11 \rightarrow 10$
1301 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1784P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	
$wR(F^2)$ = 0.078	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.08	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
1495 reflections	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
145 parameters	
All H-atom parameters refined	

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.4761 (15)	C7—O8	1.2176 (14)
C2—C3	1.5132 (16)	C7—O9	1.3110 (14)
C3—O4	1.2311 (15)	C10—O12	1.2451 (14)
C3—N5	1.3377 (16)	C10—O11	1.2588 (14)
N5—C6	1.4510 (15)	C10—C10^{i}	1.566 (2)
C6—C7	1.5081 (17)		
N1—C2—C3	110.14 (10)	O8—C7—O9	124.82 (11)
O4—C3—N5	124.09 (11)	O8—C7—C6	123.02 (11)
O4—C3—C2	121.58 (10)	O9—C7—C6	112.15 (10)
N5—C3—C2	114.31 (11)	O12—C10—O11	126.53 (11)
C3—N5—C6	122.48 (11)	O12—C10—C10^{i}	117.56 (12)
N5—C6—C7	111.24 (10)	O11—C10—C10^{i}	115.91 (12)

Symmetry code: (i) $2-x, 1-y, 1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O12^{i}	0.939 (17)	1.890 (17)	2.8163 (13)	168.7 (14)
N1—H1B···O8^{ii}	0.913 (16)	1.913 (16)	2.7934 (13)	161.3 (13)
N1—H1C···O12	0.950 (18)	1.843 (18)	2.7348 (13)	155.2 (15)
N1—H1C···O11^{iii}	0.950 (18)	2.265 (17)	2.8373 (13)	117.9 (13)
N5—H5···O4^{iv}	0.838 (16)	2.472 (16)	3.2665 (14)	158.5 (14)
O9—H9···O11^{v}	1.02 (2)	1.51 (2)	2.5310 (12)	174.3 (18)
C2—H2A···O4^{iv}	0.945 (15)	2.589 (14)	3.3022 (15)	132.5 (11)
C2—H2A···O8^{vi}	0.945 (15)	2.493 (14)	3.2024 (15)	131.9 (11)

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

Table 3
Torsion angles (°).

ψ_1	N1—C2—C3—N5	−162.80 (10)
ω	C2—C3—N5—C6	−177.94 (10)
φ_2	C3—N5—C6—C7	−145.99 (11)
ψ_{T^1}	N5—C6—C7—O9	174.46 (10)
ψ_{T^2}	N5—C6—C7—O8	−6.52 (17)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1172). Services for accessing these data are described at the back of the journal.

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