organic compounds

Cyclic water pentamers in triclinic crystals of brucinium L-glycerate

Agata Białońska,* Zbigniew Ciunik, Tomasz Popek and Tadeusz Lis

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

Correspondence e-mail: bialonsk@wcheto.chem.uni.wroc.pl

Brucinium L-glycerate 4.75-hydrate, $C_{23}H_{27}N_2O_4^+ \cdot C_3H_5O_4^- \cdot 4.75H_2O$, was obtained by racemic resolution of DL-glyceric acid. This is the first report of triclinic crystals containing brucine. The water and L-glycerate anions form tapes built up of pentamers formed by water and carboxy O atoms, and this appears to be the reason for the low symmetry of the crystal.

Comment

A special feature of water as a solvent is its ability to form aggregated hydrogen-bonded clusters, which are surrounded by non-hydrogen-bonded molecules (Scherega, 1979). Water clusters have, therefore, been the subject of a number of intense experimental and theoretical studies, as they can provide insight into fundamental biological and chemical systems. These studies have revealed ring-shaped tetramers, pentamers and hexamers as the building blocks for larger

(I)
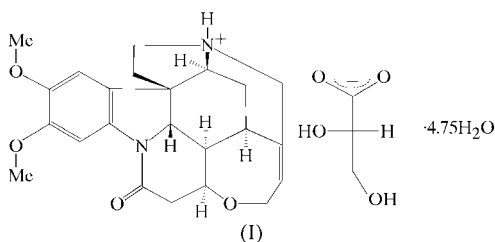
clusters (Ralf, 2001; Maheshwary *et al.*, 2001; Liu *et al.*, 1996). The lattice of a crystal host offers an attractive environment for stabilizing various topologies of water clusters, and thereby provides quantitative characterization of the hydrogen-bonding networks that exist in liquid water. Consequently, many studies have focused on the determination of the structural morphologies of water co-crystallizing with various chemical entities (Saenger, 1987; Custelcean *et al.*, 2000; Raghuraman *et al.*, 2003; Barbour *et al.*, 1998). This paper reports the structure of the title compound, (I), containing cyclic water pentamers formed between brucinium–L-glycerate ionic sheets, and the self-assembly of these pentamers into a triclinic crystalline lattice.

In the structure of (I), there are two unique brucinium glycerate ion pairs and 9.5 water molecules per unit cell. An overall view of both ion pairs with the atomic numbering scheme is presented in Fig. 1. The geometry of the brucine moieties is comparable with that found in other crystals [Cambridge Structural Database (CSD), Version 5.24 of November 2003; Allen, 2002]. The two unique L-glycerate anions have quite similar conformations, which are comparable with the molecular geometry of the glycerate anion in the crystal structure of ammonium DL-glycerate (Popek & Lis, 1996). The β-hydroxyl atom O8 (or O8A) is +synclinal and −synclinal to the α-hydroxyl atom O7 (or O7A) and atom C24 (or C24A), respectively (Table 1).

The crystal structure of (I) is composed of puckered sheets (Dijksma, Gould, Parsons & Walkinshaw, 1998) of brucine, which are separated by solvent channels consisting of L-glycerate anions and water of crystallization (Fig. 2a). The puckered sheet is constructed from common parallel corrugated ribbons.

Among numerous crystal structures, to the best of our knowledge (CSD; Allen, 2002), this is the first report of triclinic crystals containing brucine. Nevertheless, the corru-
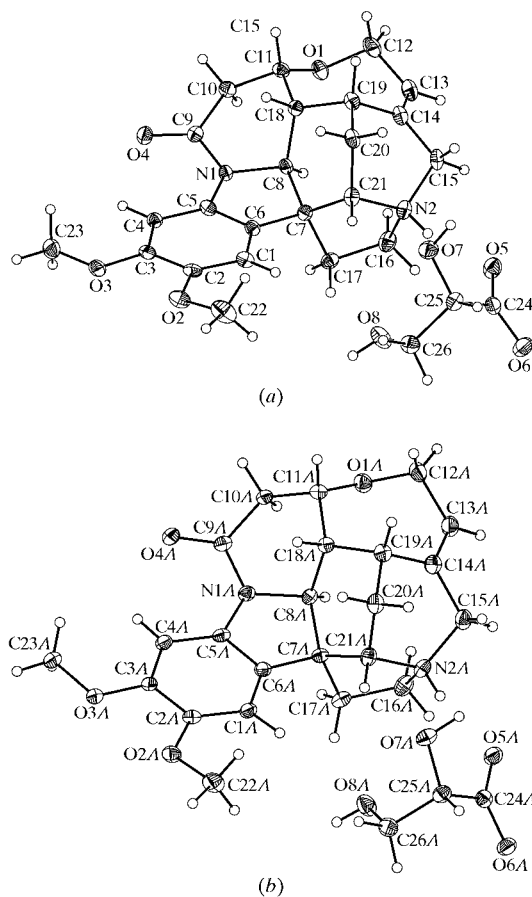

(a)

(b)

Figure 1
A view of the two brucinium glycerate ion pairs in (I), with the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

gated ribbons observed in the present structure are also present in many crystal structures in which brucine molecules are related by a twofold screw symmetry axis (Toda *et al.*, 1985; Glover *et al.*, 1985; Quinkert *et al.*, 1986; Sada *et al.*, 1998; Boiadjiev *et al.*, 1992; Wright *et al.*, 1994; Chandramohan & Ravikumar, 1999; Krajewski & Ciunik, 1999; Dijksma, Gould, Parsons, Taylor & Walkinshaw, 1998; Pinkerton *et al.*, 1993). Moreover, in the monoclinic crystals (space group *C*2) of brucinium hydrogen fumarate sesquihydrate (Dijksma, Gould, Parsons & Walkinshaw, 1998), the same puckered sheet constructed from corrugated ribbons is related by parallel alternating twofold and twofold screw-axis symmetries. In the triclinic crystal under study, molecules of the brucine puckered sheet are related by similar local twofold and twofold screw axes parallel to the [1$\bar{1}$0] direction (Fig. 2*b*). Brucine molecules *A* [at (x, y, z)] and *B* [at ($x - 1, y, z$)] of the corrugated ribbon are related by a local twofold screw axis, and brucine corrugated ribbons of the puckered sheets are related by local twofold symmetry axes. Similar C—H···O and C—H···π(arene) contacts between the two unique brucine molecules confirm the parallel alternating twofold and twofold screw axes of the puckered sheet. The close environments of both crystallographically independent brucine cations, as L-glycerate anions, are quite similar. These anions participate, *via* both their carboxy and β-hydroxyl groups, in hydrogen

bonds to the protonated amine N and carbonyl O atoms of the brucine cations (Table 2).

The carboxyl groups of both crystallographically independent anions are directed towards the solvent channel and, together with eight water molecules (O1*W*, O2*W*, O3*W*, O4*W*, O5*W*, O7*W*, O8*W* and O9*W*) form an extended tape composed of units of four hydrogen-bonded five-membered rings along the brucine corrugated ribbons of the puckered sheets (Fig. 3). In one case, the carboxyl groups of both L-glycerate anions are linked by two water bridges (O1*W* and O7*W*) and join corrugated brucine ribbons of consecutive puckered sheets. In the other case, the pentamer is composed of three water molecules (O5*W*, O7*W* and O8*W*) and two carboxy atoms (O5 and O6) of one symmetry-independent anion. Four water molecules (O1*W*, O2*W*, O4*W* and O9*W*) and only one carboxy atom (O6*A*) of the other unique anion participate in formation of the next five-membered ring. The last pentamer of the extended tape is formed by five water molecules (O2*W*, O3*W*, O4*W*, O5*W* and O8*W*).

Neighbouring water tapes are linked by the α-hydroxyl groups of the two independent anions and, together with the remaining water molecules (O6*W* and O10*W*), contribute to one four-, two five- and three six-membered rings around the tape (Fig. 4).

The existence of the pentameric ring O1*W*/O6/O7*W*/O5*A*/O6*A*, which involves the two carboxy O atoms of one independent L-glycerate anion and only one carboxy O atom of the other, causes the environment of these anions to be different and the crystal is triclinic. However, the same pentameric ring appears to determine the substructure of the water tape along the corrugated brucine ribbons as side-linked five-membered rings.
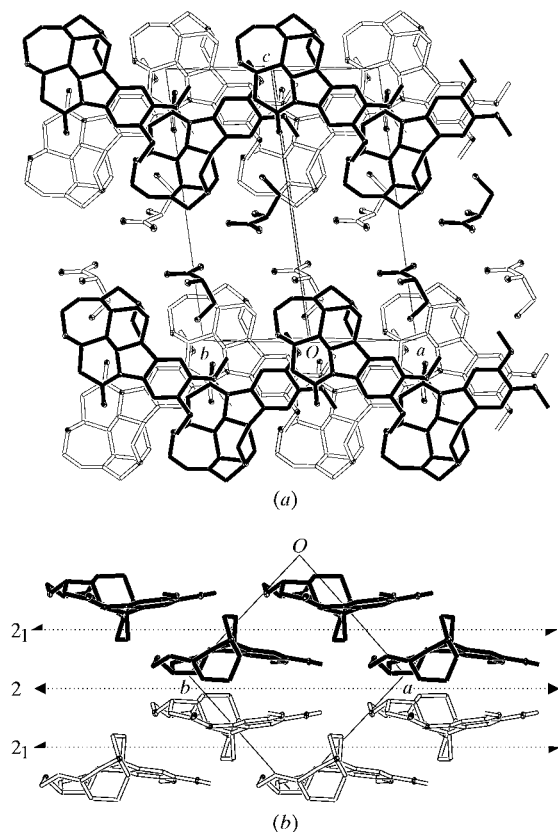

Figure 2
(*a*) The molecular packing of (I); for clarity, the water molecules have been omitted. (*b*) The local twofold and twofold screw axes of the puckered brucine sheet. Corrugated ribbons constructed of brucine puckered sheets are indicated by light and dark shading.
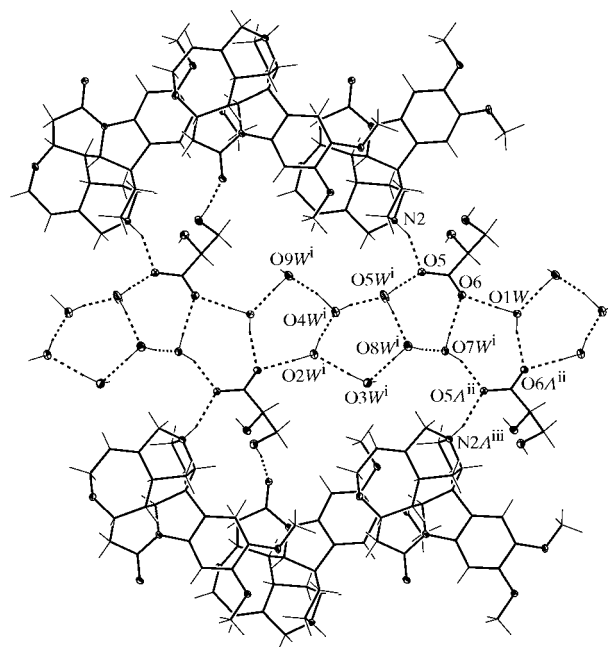

Figure 3
The water tape of five-membered rings along the corrugated brucine ribbons. [Symmetry codes: (i) $x, y - 1, z$; (ii) $x - 1, y - 1, z$; (iii) $x - 1, y - 1, z - 1$.]
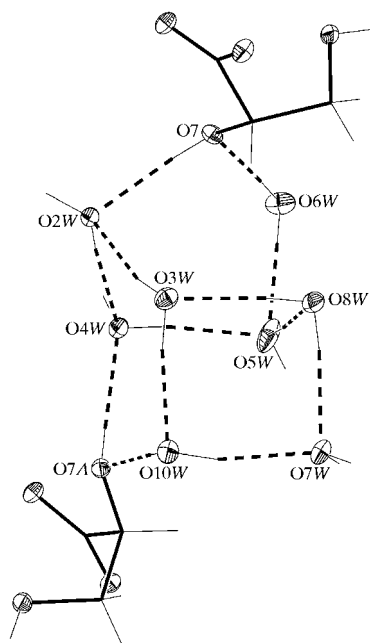
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Figure 4
The water cluster around the tape.

Experimental

The synthesis of ammonium DL-glycerate was carried out as follows. Glycerine (about 0.53 mol, 40 ml) and water (50 ml) were placed in a 250 ml flask in an ice bath. Following this, fuming nitric acid (33 ml) was added while the whole mixture was stirred vigorously and its temperature kept below 283 K. The mixture was kept at 278 K for 5 d and then the solvents were evaporated using a hot water bath. The resulting syrup was left at room temperature for 3 d. Next, water (600 ml) and lead carbonate (140 g) were added and the mixture was stirred for about 24 h. The reaction mixture was then concentrated in a hot water bath, cooled to room temperature, filtered by suction through a layer of cellite and left for crystallization. After several days, crystals of lead glycerate were separated from the mother liquor by filtration, washed with a very small quantity of a cold water–ethanol mixture (2:1) and dissolved in water, followed by the addition of excess aqueous ammonia. After vigorous stirring for several hours, the precipitate was filtered off and the solution of ammonium DL-glycerate was left for crystallization. Ammonium DL-glycerate (0.31 g, 2.5 mmol) was dissolved in a minimal quantity of water and passed through a column of Dowex-50X2 (3 × 40 cm, H$^+$ form, 100 mesh). To the resulting eluate, an equimolar quantity of brucine (POCh, Poland) was added and the solution was left for crystallization. After a few weeks, the title brucinium salt started to crystallize as colourless plates.

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_3H_5O_4^- \cdot 4.75H_2O$	$Z = 2$
$M_r = 586.11$	$D_x = 1.403$ Mg m^{-3}
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 9.308$ (3) Å	Cell parameters from 6626
$b = 9.578$ (3) Å	reflections
$c = 16.130$ (4) Å	$\theta = 3.4–28.0°$
$\alpha = 77.21$ (3)°	$\mu = 0.11$ mm^{-1}
$\beta = 87.36$ (3)°	$T = 100$ (2) K
$\gamma = 81.57$ (3)°	Plate, colourless
$V = 1387.1$ (7) Å^3	$0.75 \times 0.30 \times 0.07$ mm

Data collection

Kuma KM-4 CCD diffractometer	$\theta_{max} = 28.0°$
ω scans	$h = -12 \rightarrow 12$
16 810 measured reflections	$k = -12 \rightarrow 12$
6655 independent reflections	$l = -21 \rightarrow 20$
5944 reflections with $I > 2\sigma(I)$	
$R_{int} = 0.045$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.00$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
6655 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
739 parameters	
H-atom parameters constrained	

Table 1
Selected torsion angles (°) of the two independent L-glycerate anions in the structure of (I).

O5—C24—C25—O7	−8.3 (3)	O5A—C24A—C25A—O7A	−11.6 (3)
O5—C24—C25—C26	111.9 (3)	O5A—C24A—C25A—C26A	108.8 (2)
O6—C24—C25—O7	171.4 (2)	O6A—C24A—C25A—O7A	168.4 (2)
O6—C24—C25—C26	−68.4 (3)	O6A—C24A—C25A—C26A	−71.2 (3)
O7—C25—C26—O8	65.1 (2)	O7A—C25A—C26A—O8A	67.1 (2)
C24—C25—C26—O8	−57.9 (3)	C24A—C25A—C26A—O8A	−55.9 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O5	1.00	1.78	2.694 (3)	151
N2—H2$\cdots$O7	1.00	2.38	3.075 (3)	126
N2A—H2A$\cdots$O5A^i	0.89	1.88	2.738 (3)	163
O7—H71$\cdots$O2W	0.86	1.85	2.711 (3)	177
O8—H81$\cdots$O4A^{ii}	0.85	2.01	2.835 (3)	166
O7A—H72$\cdots$O4W	0.93	1.89	2.766 (3)	156
O8A—H82$\cdots$O4^{iii}	0.84	1.98	2.806 (2)	167
O1W—H11W$\cdots$O6	0.93	1.77	2.698 (3)	176
O1W—H12W$\cdots$O6A^{iv}	0.86	1.92	2.750 (3)	161
O2W—H21W$\cdots$O6A^v	0.90	1.82	2.714 (3)	175
O2W—H22W$\cdots$O4W	0.89	1.96	2.832 (3)	169
O3W—H31W$\cdots$O2W	0.90	1.91	2.798 (3)	165
O3W—H32W$\cdots$O10W	0.91	1.90	2.804 (3)	172
O4W—H41W$\cdots$O5W	0.90	1.85	2.738 (3)	169
O4W—H42W$\cdots$O9W	0.99	1.76	2.730 (3)	165
O5W—H51W$\cdots$O8W	0.89	2.03	2.919 (3)	176
O5W—H52W$\cdots$O5^{vi}	0.99	1.74	2.706 (3)	166
O6W—H61W$\cdots$O5W	0.82	1.78	2.590 (5)	173
O6W—H62W$\cdots$O7	0.94	1.84	2.781 (4)	176
O7W—H71W$\cdots$O6^{vi}	0.87	1.87	2.736 (3)	176
O7W—H72W$\cdots$O5A^{ii}	0.85	1.92	2.731 (3)	159
O8W—H81W$\cdots$O7W	0.93	1.83	2.743 (3)	166
O8W—H82W$\cdots$O3W	0.92	1.88	2.796 (3)	174
O9W—H91W$\cdots$O1W^{vii}	0.96	1.73	2.683 (3)	177
O9W—H92W$\cdots$O8W^{vii}	0.86	2.01	2.869 (3)	178
O10W—H1W$\cdots$O7W	0.92	1.88	2.786 (3)	169
O10W—H2W$\cdots$O7A	0.90	1.91	2.807 (3)	176

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

H atoms were found in $\Delta\rho$ maps. The H-atom parameters were refined with isotropic displacement parameters and were fixed before the final cycle of refinement. Friedel pairs were merged before the final refinement. The absolute configuration of (I) was chosen on the basis of the known absolute configuration of brucine. The site-zoccupancy factor for the water molecule O6W/H61W/H62W was refined and fixed at 0.5.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

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