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Cytosinium *N*-benzoylglycinate monohydrate, a redetermination at 105 K

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.001 Å
R factor = 0.033
wR factor = 0.092
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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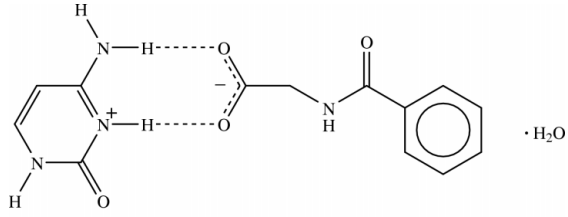
The crystal structure of the title complex, $C_4H_6N_3O^+\cdot C_9H_8NO_3^-\cdot H_2O$, has been redetermined as part of an electron paramagnetic resonance (EPR) study of the effect of radiation on such systems. Protonated cytosine and the deprotonated carboxylate group of the amino acid form a typical eight-membered hydrogen-bonded ring motif.

Comment

The physical and chemical alterations of DNA induced by ionizing radiation are significantly influenced by the environment of the macromolecule, such as the degree of hydration, the possible presence of various radiation-modifying agents and the extent of molecular packing and complexation with nuclear proteins (histones) (Becker & Sevilla, 1998). In particular, the possible modifying action of histones on the DNA radiation response is important (Weiland & Hüttermann, 2000). Model studies of crystalline 1:1 complexes of a peptide and a nucleic acid constituent are useful for understanding mechanisms for charge transfer between the partners of the complex following the radiation-induced charge injection. For the purpose of electron paramagnetic resonance (EPR) studies of the effect of radiation on such systems, single crystals are the preferred type of sample. The crystal structure of the *N*-benzoylglycine (hippuric acid)–cytosine complex (obtained as a monohydrate), (I), had been determined previously by Tamura *et al.* (1972). The *R* factor is, however, high by current standards (0.131) and several H atoms are missing or have obviously inaccurate positions. Hence, a new structure analysis was undertaken, providing an improved set of cell parameters as well as structural data of much higher precision.



(I)

The structure of (I) is shown in Fig. 1. The bond lengths (Table 1) and angles of protonated cytosine correspond closely to those observed in the structure of cytosine hydrochloride (Mandel, 1977), as well as in other structures with protonated cytosine. The cytosinium–carboxylate interaction with two

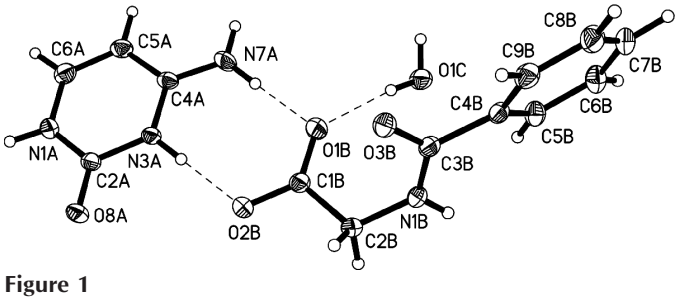


Figure 1
The molecular structure of the cytosinium *N*-benzoylglycinate monohydrate complex. Displacement ellipsoids are shown at the 50% probability level, H atoms are shown as spheres of arbitrary size and hydrogen bonding is indicated by dashed lines.

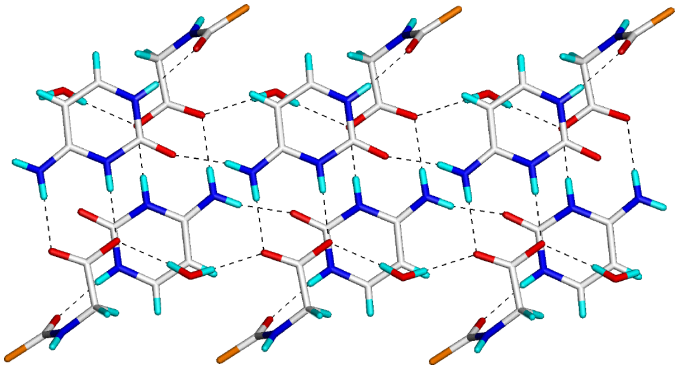


Figure 2
View of a flat tube generated by hydrogen bonding. For clarity, only atom C4*B*, coloured orange, is shown for the phenyl rings of *N*-benzoylglycine. The *b* axis is vertical and hydrogen bonding is indicated by dashed lines.

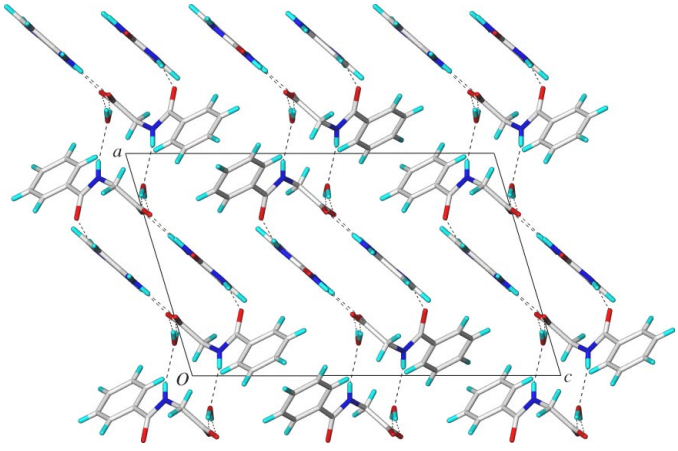


Figure 3
The molecular packing and unit cell viewed along the *b* axis. Hydrogen bonding is indicated by dashed lines.

hydrogen bonds (Fig. 1) is a motif observed in all cytosine complexes contained in the Cambridge Structural Database (Version 5.25; Allen, 2002) where the co-crystallized organic anion contains a carboxylate group. These include *N*-formylglycinate (Ohki *et al.*, 1975), hydrogen maleate (Balasubramanian *et al.*, 1996), trichloroacetate (Gdanic *et al.*, 1989) and *N*,*N*-phthaloyl–DL-glutamate (Takenaka *et al.*, 1980). Cytosine–amino acid pairs are connected by a direct H72*A*$\cdots$O8*A*$(x, y-1, z)$ hydrogen bond and a bridging water molecule to form extended chains along the *b* axis. Two such chains are then joined by N1*A*—H1*A*$\cdots$O3*B*$(1-x, 2-y, 1-z)$ hydrogen bonds to form a flat tube-like arrangement, as shown in Fig. 2. One more strong hydrogen bond (N1*B*—H1*B*) connects the tubes and completes the two-dimensional hydrogen-bonding pattern (Fig. 3). The herring-bone stacking of aromatic rings gives rise to several close C—H$\cdots$C contacts, the shortest being C7*B*—H7$\cdots$C4*B*$(x, \frac{3}{2}-y, \frac{1}{2}+z)$ at 2.846 Å.

Experimental

N-Benzoylglycine and cytosine monohydrate were obtained from Sigma–Aldrich. Colorless needle-shaped crystals were prepared by slow evaporation of 1:1 (*v*/*v*) methanol–water solutions at room temperature or at 308 K.

Crystal data

$C_4H_6N_3O^+\cdot C_9H_8NO_3^-\cdot H_2O$
M_r = 308.30
Monoclinic, $P2_1/c$
a = 11.4821 (2) Å
b = 7.2107 (1) Å
c = 18.2817 (3) Å
β = 106.692 (1)°
V = 1449.83 (4) Å^3
Z = 4
D_x = 1.412 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6264 reflections
θ = 1.9–28.3°
μ = 0.11 mm^{-1}
T = 105 (2) K
Block, colourless
1.05 × 0.95 × 0.22 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.816, T_{max} = 0.976
13211 measured reflections
3603 independent reflections
3354 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 28.3°
$h = -15 \rightarrow 14$
$k = -9 \rightarrow 9$
$l = -19 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
S = 1.03
3603 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.4875P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.012
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0199 (18)

Table 1
Selected geometric parameters (Å, °).

O8*A*—C2*A*	1.2228 (12)	C5*A*—C6*A*	1.3482 (14)
N1*A*—C6*A*	1.3675 (13)	O1*B*—C1*B*	1.2497 (12)
N1*A*—C2*A*	1.3675 (13)	O2*B*—C1*B*	1.2681 (12)
N3*A*—C4*A*	1.3613 (11)	O3*B*—C3*B*	1.2476 (12)
N3*A*—C2*A*	1.3786 (12)	N1*B*—C3*B*	1.3379 (12)
N7*A*—C4*A*	1.3077 (13)	N1*B*—C2*B*	1.4457 (12)
C4*A*—C5*A*	1.4299 (13)		
O1*B*—C1*B*—C2*B*—N1*B*	6.87 (13)	C2*B*—N1*B*—C3*B*—C4*B*	−173.84 (8)
O2*B*—C1*B*—C2*B*—N1*B*	−173.87 (8)	N1*B*—C3*B*—C4*B*—C5*B*	25.23 (13)
C1*B*—C2*B*—N1*B*—C3*B*	70.48 (12)	N1*B*—C3*B*—C4*B*—C9*B*	−156.93 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O3B^{i}	0.880 (15)	1.887 (15)	2.7595 (11)	170.8 (13)
N3A—H3A···O2B	0.913 (14)	1.799 (14)	2.7121 (11)	178.1 (12)
N7A—H71A···O1B	0.925 (15)	1.829 (15)	2.7543 (12)	179.3 (14)
N7A—H72A···O8A^{ii}	0.880 (16)	1.897 (16)	2.7576 (11)	165.6 (14)
C5A—H5A···O3B^{iii}	0.953 (14)	2.496 (14)	3.4128 (12)	161.3 (11)
N1B—H1B···O1C^{iv}	0.803 (15)	2.096 (15)	2.8453 (11)	155.4 (13)
O1C—H11C···O1B	0.861 (17)	1.968 (17)	2.8163 (10)	168.5 (15)
O1C—H12C···O2B^{ii}	0.874 (17)	2.039 (17)	2.8998 (10)	168.1 (15)

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1-y, 1-z$.

Positional parameters were refined for H atoms bonded to O, N and C5*A*, which are involved in hydrogen bonds, as well as for the methylene H atoms of *N*-benzoylglycinate. Atom H6*A* and the aromatic H atoms of *N*-benzoylglycine were positioned with idealized geometry and fixed C—H distances (0.95 Å). U_{iso} values were fixed at $1.2U_{eq}$ of the carrier atom for the cytosinium and *N*-benzoylglycinate molecules and $1.5U_{eq}$ for the water molecule.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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