organic papers

A hydrate of carbamoylmethyl 3,4,5-trihydroxy-benzoate with three different molecular conformations

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The crystal structure of carbamoylmethyl 3,4,5-trihydroxy-benzoate 0.33-hydrate, $C_9H_9NO_6\cdot0.33H_2O$, is reported. Three crystallographically independent molecules with different conformations are observed, with two having the amide group in the plane of the benzoate unit and the third lying out of the plane.

Comment

The title compound, (I), crystallizes with three molecules of carbamoylmethyl 3,4,5-trihydroxybenzoate and one molecule of water in the asymmetric unit. Unusually, all three crystallographically independent molecules of the organic compound adopt different conformations (Fig. 1).

Two of the molecules are approximately planar, the only difference between them being the positions of the phenolic H atoms. A third molecule has the amide group lying nearly perpendicular to the plane of the gallate (3,4,5-trihydroxybenzoate), with a dihedral angle between the benzoate and amide planes of 70.80 (7)°.
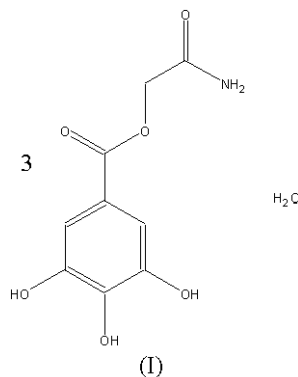
With each of the molecules possessing five hydrogen-bond donor groups and six acceptor atoms, many different hydrogen-bonding combinations are possible. Graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), using only hydrogen bonds with an H–acceptor distance of 2.5 Å or less (Table 1) is used to characterize the hydrogen-bond patterns. The molecules adopt a pattern of chains of crystallographically identical molecules linked by hydrogen bonds. Each chain is crosslinked to other chains of crystallographically independent molecules to form sheets, in which the water molecules are inserted (Fig. 2; symmetry-related molecules are shown in the same colour). Two types of intramolecular pattern are observed, both $S_1^1(5)$. The first of these is observed in all three crystallographically independent molecules, being formed by the adjacent hydroxyl groups. Two of these interactions are observed in each of molecules *B* and *C*, with only one in the
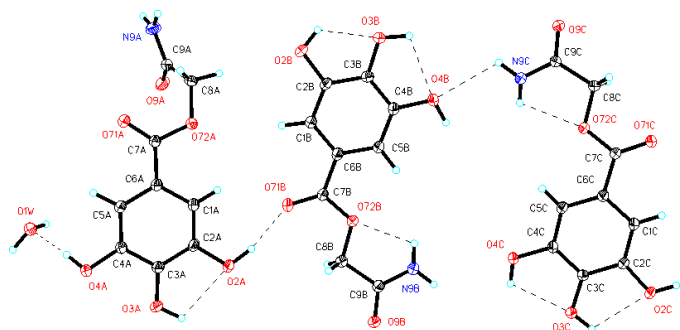
Figure 1
The asymmetric unit of the title compound, showing the atom labels used in tables and figures. Displacement ellipsoids are shown at the 30% probability level.
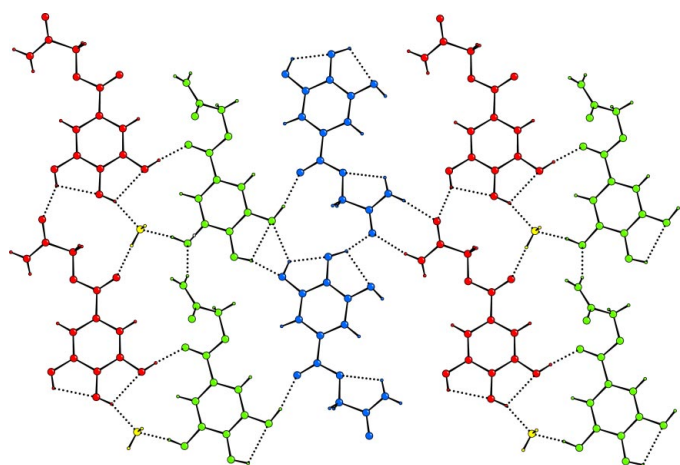

Figure 2
The hydrogen-bonded sheet. The three crystallographically independent molecules C1A to N9A, C1B to N9B, and C1C to N9C, are shown in green, blue and red, respectively. The water molecule is shown in yellow.
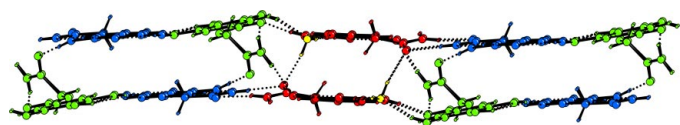

Figure 3
The linking of the sheets by the water (yellow) and the non-planar conformer of the title molecule (green). The colour scheme used is identical to that in Fig. 2.
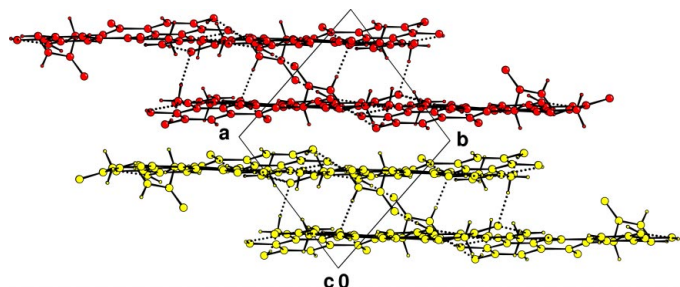

Figure 4
The double-layers of sheets are not connected by any hydrogen bonds.

non-planar molecule A. The second $S_1^1(5)$ pattern is observed only in molecules B and C, and is formed by the amide–ester N—H···O interaction. Both the blue and red chains containing the planar molecular units (molecules B and C, respectively) are linked by phenol–amide O—H···O hydrogen bonds, with the red molecules forming $C_1^1(10)$ chains and the blue molecules forming $C_1^1(11)$ chains, the difference arising from which hydroxyl moiety is involved. The green non-planar molecules (molecule A) are linked by amide–phenol N—H···O hydrogen bonds in a $C_1^1(10)$ chain. The red and blue chains are linked in the sheet by $R_2^2(8)$ patterns formed by amide–amide N—H···O hydrogen bonds. The green and blue chains are linked in the sheet by $C_2^2(9)$ patterns formed by hydroxyl–carbonyl and hydroxyl–hydroxyl O—H···O hydrogen bonds. A second hydroxyl–hydroxyl inter-action forms $R_2^2(7)$ and $R_3^3(14)$ patterns with these groups. The red and green chains are connected directly and through the water molecule, giving rise to three ring graph sets, viz. $R_2^3(14)$, $R_3^3(14)$ and $R_4^4(18)$.

Links between sheets form double layers and these are provided by the three hydrogen bonds O1W—H2W···O9C^{iv}, N9A—H92A···O4C^{iv} and O4B—H4B···O9A^{v} (Fig. 3; see Table 1 for symmetry codes). No hydrogen bonds are observed between adjacent double layers (Fig. 4).

Experimental

The title compound was synthesized by the method of Christiansen (1926). A single crystal suitable for X-ray diffraction was grown by the slow diffusion of diethyl ether into an ethanol solution.

Crystal data

$C_9H_9NO_6\cdot0.33H_2O$	$Z = 6$
$M_r = 233.18$	$D_x = 1.639$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 8.266$ (5) Å	Cell parameters from 54
$b = 8.515$ (4) Å	reflections
$c = 20.614$ (7) Å	$\theta = 20$–22°
$\alpha = 87.08$ (3)°	$\mu = 1.23$ mm^{-1}
$\beta = 86.56$ (3)°	$T = 220$ (2) K
$\gamma = 78.32$ (3)°	Prism, colourless
$V = 1417.2$ (12) Å^3	$0.62 \times 0.28 \times 0.24$ mm

Data collection

Stoe Stadi-4 four-circle diffractometer	$R_{int} = 0.020$
ω–θ scans	$\theta_{max} = 69.9°$
Absorption correction: numerical	$h = -9 \rightarrow 10$
(*SHELXTL*; Sheldrick, 1997)	$k = -10 \rightarrow 10$
$T_{min} = 0.617$, $T_{max} = 0.777$	$l = -20 \rightarrow 25$
8429 measured reflections	3 standard reflections
5000 independent reflections	frequency: 60 min
4192 reflections with $I > 2\sigma(I)$	intensity decay: 7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.3171P]$
$wR(F^2) = 0.122$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
5000 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
511 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: *SHELXTL*
	Extinction coefficient: 0.0019 (4)

Table 1
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O2A—H2A$\cdots$O71B^{i}	0.96 (3)	1.99 (3)	2.931 (2)	165 (3)
O3A—H3A$\cdots$O2A	0.93 (4)	2.34 (3)	2.766 (2)	107 (3)
O3A—H3A$\cdots$O2B^{ii}	0.93 (4)	1.91 (4)	2.807 (2)	163 (3)
O4A—H4A$\cdots$O1W	0.87 (4)	1.91 (4)	2.746 (2)	160 (3)
N9A—H91A$\cdots$O4A^{iii}	0.97 (3)	2.07 (3)	2.978 (3)	156 (3)
N9A—H92A$\cdots$O4C^{iv}	0.94 (3)	2.01 (3)	2.950 (3)	176 (3)
O2B—H2B$\cdots$O3B	0.89 (3)	2.06 (3)	2.631 (2)	121 (3)
O2B—H2B$\cdots$O2A^{ii}	0.89 (3)	2.31 (3)	2.975 (3)	131 (3)
O3B—H3B$\cdots$O4B	1.02 (4)	2.31 (4)	2.754 (2)	105 (2)
O3B—H3B$\cdots$O9B^{v}	1.02 (4)	1.61 (4)	2.607 (2)	164 (3)
O4B—H4B$\cdots$O9A^{v}	0.94 (3)	1.71 (3)	2.649 (2)	177 (3)
N9B—H91B$\cdots$O72B	0.85 (3)	2.23 (3)	2.645 (2)	111 (3)
N9B—H92B$\cdots$O9C^{iv}	0.93 (3)	2.06 (3)	2.986 (2)	172 (2)
O2C—H2C$\cdots$O71A^{vi}	0.87 (3)	1.83 (3)	2.688 (2)	172 (3)
O3C—H3C$\cdots$O2C	0.87 (3)	2.29 (3)	2.707 (2)	110 (3)
O3C—H3C$\cdots$O1W^{vi}	0.87 (3)	2.01 (3)	2.817 (2)	155 (3)
O4C—H4C$\cdots$O3C	0.84 (3)	2.28 (3)	2.697 (2)	111 (2)
O4C—H4C$\cdots$O9C^{iii}	0.84 (3)	2.03 (3)	2.772 (2)	147 (2)
N9C—H91C$\cdots$O4B^{vii}	0.91 (3)	2.48 (3)	2.984 (2)	115 (2)
N9C—H91C$\cdots$O9B^{viii}	0.91 (3)	2.05 (3)	2.943 (3)	167 (3)
N9C—H92C$\cdots$O72C	0.85 (3)	2.30 (2)	2.665 (2)	106 (2)
O1W—H1W$\cdots$O71C^{ix}	0.95 (3)	1.86 (3)	2.807 (2)	173 (3)
O1W—H2W$\cdots$O9C^{iv}	0.87 (3)	1.99 (3)	2.852 (2)	171 (3)

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

H atoms bound to carbon were placed in calculated positions and refined as riding or rotating groups. The amide, hydroxyl and water H atoms were located in a difference map and freely refined, giving N—H bond lengths between 0.85 (3) and 0.97 (3) Å, and O—H bond lengths between 0.84 (3) and 1.02 (4) Å.

Data collection: *DIF*4 (Stoe & Cie, 1990); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXTL*.

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