

## Melaminium benzoate dihydrate

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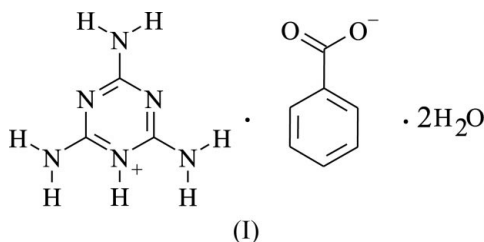
## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.036  
 $wR$  factor = 0.094  
Data-to-parameter ratio = 14.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A new melaminium salt, 2,4,6-triamino-1,3,5-triazin-1-ium benzoate dihydrate,  $\text{C}_3\text{H}_7\text{N}_6^+ \cdot \text{C}_6\text{H}_5\text{COO}^- \cdot 2\text{H}_2\text{O}$ , consists of singly protonated melaminium residues, benzoate anions and water molecules. The components are linked by hydrogen bonds into a three-dimensional framework structure. The melaminium residues are connected by two pairs of  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonds into chains. The benzoate anion acts as acceptor for two hydrogen bonds from melaminium residues and for three hydrogen bonds from the two water molecules, which themselves form an  $\text{O}-\text{H} \cdots \text{O}$  bonded dimeric structure. The extended structure is a double layer, with a distance of  $3.38(1)\text{ \AA}$  between the triazine rings, indicating  $\pi-\pi$  interactions.

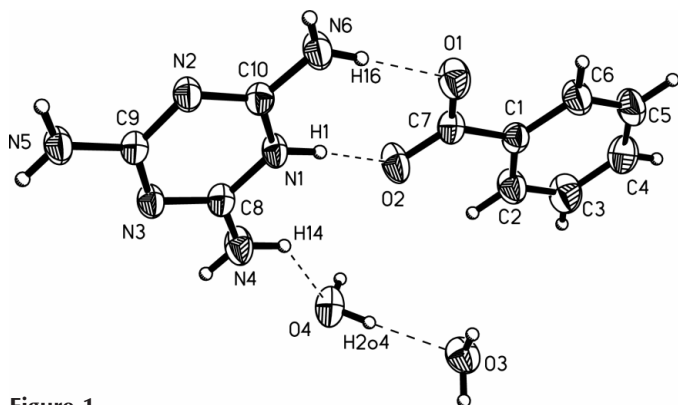
## Comment

The present study is a continuation of our investigations characterizing the hydrogen-bonding system formed by triazine derivatives in the solid state (Janczak & Perpétuo, 2004). Melamine and its organic and inorganic complexes or salts can develop supramolecular structures *via* multiple hydrogen bonds containing components that contain complementary arrays of hydrogen bonding sites (Desiraju, 1990; MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). In order to expand the understanding of the solid-state physical-organic chemistry of compounds that form multiple  $\text{N}-\text{H} \cdots \text{N}$ ,  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{O}$  hydrogen-bonding systems, we present here the solid-state structure of melaminium benzoate dihydrate, (I).

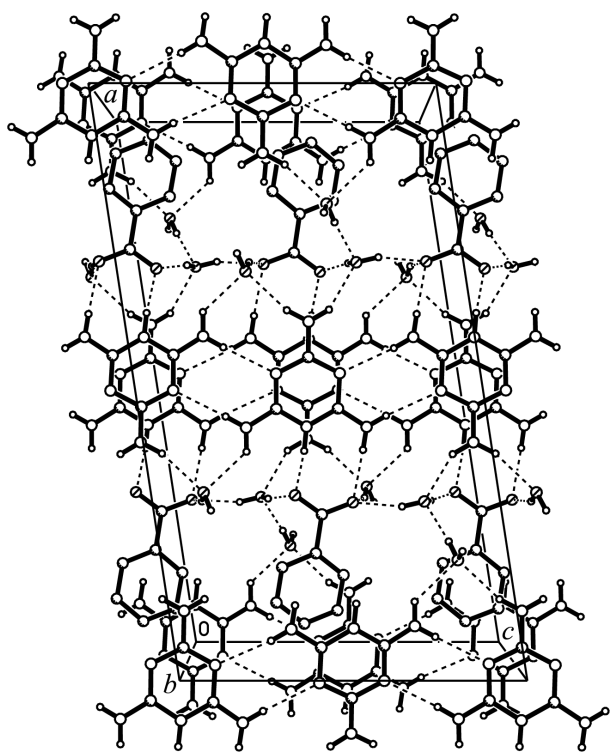


The asymmetric unit of (I) consists of a melaminium cation, singly protonated at the one ring N atom, a benzoate anion and two water molecules that form a dimer with an  $\text{O} \cdots \text{O}$  distance of  $2.862(2)\text{ \AA}$  (Fig. 1). The melaminium ring is essentially planar [the deviation of the N and C atoms from the mean plane is smaller than  $0.014(2)\text{ \AA}$ ], but exhibits significant distortions from the ideal hexagonal form (Table 1). The internal  $\text{C}-\text{N}-\text{C}$  angle at the protonated N atom in the melaminium cation is greater than the other two  $\text{C}-\text{N}-\text{C}$  angles within the ring. This distortion results from the steric effect of a lone pair of electrons, predicted by the valence-shell

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**Figure 1**  
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii. Dashed lines represent hydrogen bonds.



**Figure 2**  
The crystal packing, showing the stacking structure of hydrogen-bonded melaminium and benzoate residues that stabilize the N—H···O and O—H···O hydrogen bonds. Dashed lines represent hydrogen bonds.

electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992). A search of the Cambridge Structural Database (Allen, 2002) for the structures containing singly protonated melaminium residues shows 15 structures; all these structures show melaminium ring distortions very similar to those found in the present structure.

The C—C bond lengths and C—C—C angles of the benzoate ion are slightly perturbed from hexagonal symmetry due to the substitution effect of the carboxylate group. The O—C—O angle of the carboxylate group is greater than 120° because of the steric effect of lone-pair electrons on both O atoms. The bond lengths in the deprotonated carboxyl group are almost identical and intermediate between the single

$Csp^2-O$  (1.308–1.320 Å) and double  $Csp^2=O$  bond lengths (1.214–1.224 Å; Allen *et al.*, 1987), indicating delocalization of the charge over both O atoms of the  $COO^-$  group.

An extensive series of hydrogen bonds (Table 2) links the components of (I). Each melaminium residue is involved in nine hydrogen bonds; in seven of these it acts as a donor and in the remaining two as an acceptor. Two pairs of N—H···N hydrogen bonds link the melaminium cations related by the twofold axis and translation, to form chains parallel to [001]; The interaction of singly protonated melaminium residues in melaminium citrate, in contrast, involves centrosymmetric hydrogen-bonded dimers (Perpétuo & Janczak, 2003). Two N—H···O hydrogen bonds (Table 2) link each melaminium cation to the benzoate anion of the asymmetric unit (Fig. 1), whereby the cation and anion are almost coplanar (interplanar angle 2.7 (1)°), and two N—H···O hydrogen bonds are formed to water acceptors. Three N—H···O hydrogen bonds are formed from melaminium to the water molecules.

The benzoate anion acts as acceptor for two hydrogen bonds from melaminium residues and for three hydrogen bonds from the two water molecules. The water molecules interact directly forming a hydrogen-bonded dimeric structure (Fig. 1); thus, each water molecule is involved in a total of four hydrogen bonds, in two as donor and in two as acceptor.

The net effect of all the hydrogen bonds is to form a three-dimensional network; however, disregarding the hydrogen bond  $H_2O_4 \cdots O_3$ , the extended structure is a double layer parallel to the (010) plane (see Fig. 2). Within one double layer, the melaminium rings are separated by 3.38 (1) Å, indicating  $\pi-\pi$  interactions (Pauling, 1960). The double layers are not further associated, because they are additionally separated by benzoate anions, with a long distance of 6.55 (1) Å.

## Experimental

Melamine and benzoic acid in the molar ratio 1:1 were dissolved in boiling water and the solution was cooled to room temperature. After several days, colourless single crystals appeared.

### Crystal data



$M_r = 284.29$

Monoclinic,  $C2/c$

$a = 21.473$  (4) Å

$b = 10.229$  (2) Å

$c = 12.353$  (2) Å

$\beta = 98.68$  (2)°

$V = 2682.2$  (9) Å<sup>3</sup>

$Z = 8$

$D_x = 1.408$  Mg m<sup>-3</sup>

$D_m = 1.40$  Mg m<sup>-3</sup>

Density measured by flotation in

chloroform/dichloromethane

Mo  $K\alpha$  radiation

Cell parameters from 2015

reflections

$\theta = 3.3-28.0^\circ$

$\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  (2) K

Parallelepiped, colourless

$0.45 \times 0.42 \times 0.24$  mm

### Data collection

Kuma KM-4 diffractometer with  
CCD area detector

$\omega$  scans

Absorption correction: analytical  
face-indexed (SHELXTL;  
Sheldrick, 1990)

$T_{\min} = 0.948$ ,  $T_{\max} = 0.970$

15755 measured reflections

3218 independent reflections

2015 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\text{max}} = 28.0^\circ$

$h = -27 \rightarrow 28$

$k = -10 \rightarrow 13$

$l = -16 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.094$   
 $S = 1.00$   
 3218 reflections  
 218 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0025 (4)

Table 1

Selected geometric parameters (Å, °).

N1–C8	1.3512 (14)	C9–N5	1.3262 (14)
N1–C10	1.3625 (15)	C9–N3	1.3502 (14)
C8–N4	1.3190 (15)	C10–N6	1.3149 (15)
C8–N3	1.3282 (13)	O1–C7	1.2565 (14)
N2–C10	1.3324 (14)	O2–C7	1.2537 (14)
N2–C9	1.3524 (14)		
C8–N1–C10	119.54 (10)	C8–N3–C9	115.60 (10)
C10–N2–C9	115.26 (10)	O2–C7–O1	123.32 (11)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1 $\cdots$ O2	0.935 (14)	1.733 (14)	2.6649 (13)	173.6 (12)
N4–H14 $\cdots$ O4	0.906 (14)	2.194 (14)	2.8771 (15)	131.7 (12)
N4–H24 $\cdots$ N3 <sup>i</sup>	0.874 (15)	2.187 (16)	3.0473 (16)	167.7 (13)
N5–H15 $\cdots$ O3 <sup>ii</sup>	0.889 (14)	2.110 (13)	2.9173 (16)	150.6 (12)
N5–H25 $\cdots$ O4 <sup>i</sup>	0.916 (14)	2.119 (14)	2.9923 (16)	158.9 (11)
N6–H16 $\cdots$ O1	0.883 (14)	2.037 (15)	2.9191 (15)	178.0 (13)
N6–H26 $\cdots$ N2 <sup>iii</sup>	0.842 (13)	2.292 (14)	3.1228 (16)	169.0 (12)
O3–H1O3 $\cdots$ O1 <sup>iv</sup>	0.854 (17)	1.918 (18)	2.7349 (14)	159.5 (16)
O3–H2O3 $\cdots$ O2 <sup>v</sup>	0.881 (16)	1.974 (16)	2.8329 (14)	164.6 (16)
O4–H1O4 $\cdots$ O1 <sup>vi</sup>	0.874 (18)	2.091 (19)	2.9045 (18)	154.7 (17)
O4–H2O4 $\cdots$ O3	0.863 (18)	2.001 (18)	2.8621 (16)	175.5 (15)

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

H atoms of the benzoate ring were included using a riding model, with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the parent C atoms and C–H = 0.93 Å. The H atoms of the melaminium cation and water molecules were located in the difference Fourier map and their positions were refined, with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N,O})$ .

Data collection: *KM-4 CCD Software* (Kuma, 2002); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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