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Melaminium glutarate monohydrate

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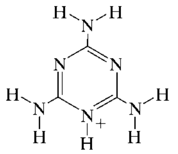
The crystal structure of the title new melaminium salt, 2,4,6-triamino-1,3,5-triazin-1-ium glutarate monohydrate, $C_3H_7N_6^+\cdot C_5H_7O_4^-\cdot H_2O$, is built up from singly protonated melaminium residues, mono-dissociated glutarate ions and water molecules. The melaminium residues are interconnected by four N—H⋯N hydrogen bonds to form chains. These chains of melaminium residues form a stacking structure. The glutarate anions form a hydrogen-bonded zigzag polymer of the form $[\cdots HOOC(CH_2)_3COO\cdots HOOC(CH_2)_3COO\cdots]_n$. The oppositely charged moieties, *i.e.* the melaminium and glutarate chains, form two-dimensional polymeric sheets. These sheets are interconnected by O—H⋯O hydrogen bonds between the COO^- moieties and the water molecules, and these hydrogen bonds stabilize the stacking structure.

Comment

This study is a continuation of our investigation into the characterization of the hydrogen bonds formed by melamine in the solid state (Janczak & Perpétuo, 2001*a*,*b*,*c*,*d*; Perpétuo & Janczak, 2002). Melamine, as well as its organic and inorganic complexes or salts, can develop supramolecular structures *via* multiple hydrogen bonds by self-assembly of components which contain complementary arrays of hydrogen-bonding sites (MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). To expand the understanding of the solid-state physical-organic chemistry of compounds containing multiple and other hydrogen-bonding systems, we present herein the solid-state structure of singly protonated melaminium glutarate monohydrate, (I). Additionally, the geometries of both oppositely charged parts, *i.e.* the singly protonated melaminium cation and the glutarate anion, are compared with the *ab initio* fully optimized parameters calculated at the HF/6-31G(*d*,*p*) level (Frisch *et al.*, 1995). The *ab initio* molecular-orbital calculations were carried out on the isolated ions, and the results are illustrated in Fig. 1.

The asymmetric unit of (I) consists of one melaminium residue protonated at one of the three ring N atoms, one glutarate anion and one water molecule (Fig. 2). The six-membered aromatic ring of the singly protonated melaminium residue exhibits significant distortions from the ideal hexagonal form. The internal C—N—C angle at the protonated N atom is greater than the other two C—N—C angles within the ring. This is a result of the steric effect of a lone-pair electron, predicted by the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992). As a result of the protonation of the melamine ring at one N atom, the internal N—C—N angle involving only non-protonated N atoms is significantly greater than the N—C—N angles involving both protonated and non-protonated N atoms. The correlation between the internal C—N—C angles within the melaminium ring is similar to those reported for the crystals of barbituric acid with melamine (Zerkowski *et al.*, 1994), melaminium phthalate (Janczak & Perpétuo, 2001*a*), melaminium chloride hemihydrate (Janczak & Perpétuo, 2001*c*), bis(melaminium) sulfate dihydrate (Janczak & Perpétuo, 2001*d*) and melaminium acetate monohydrate acetic acid solvate (Perpétuo & Janczak, 2002), *i.e.*, those singly protonated melaminium salts that have been previously structurally characterized. The *ab initio* optimized geometry calculated for the singly protonated melaminium residue in (I) (see Fig. 1*a*) shows a similar correlation between the C—N—C and N—C—N angles within the ring to that seen in the crystal. Thus, the ring distortion of the singly protonated melaminium residue results mainly from the protonation and, to a lesser degree, from the hydrogen-bonding system and crystal packing. The C—N bond lengths within the ring in the optimized melaminium residue are slightly shorter than those in the crystal of (I), while the C—N bond lengths which join the amine groups are quite similar in both treatments. The lengthening of the C—N bonds in the melaminium ring in the crystal is likely to be due to interaction of the π–π clouds between the rings in the stack.



$\cdot HOOC(CH_2)_3COO^-\cdot H_2O$

(I)

The melaminium residue in the crystal of (I) is involved in nine hydrogen bonds, in seven as donor and in the remaining two as acceptor. A pair of almost linear N—H⋯N bonds links the melaminium residue with two neighbouring melaminium residues to form a chain (Fig. 3) that is inclined by ~39, ~21 and ~44° to the *a*, *b* and *c* axes, respectively. The remaining five very bent N—H⋯O bonds link the chains of melaminium residues with the glutarate anions and the water molecule.

The glutarate anion is involved in seven hydrogen bonds, in six as acceptor and in one as donor. Atoms O1, O2 and O3 are involved in two hydrogen bonds as acceptors, while atom O4 is a donor. The C—O bond lengths in the ionized carboxyl group

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are intermediate between single Csp^2—O and double Csp^2═O distances (1.247–1.262 Å; Allen *et al.*, 1987), indicating delocalization of the charge on both O atoms. The slight difference between the C4—O1 and C4—O2 bond lengths correlates well with the strength of the hydrogen bonds in which the O atoms are involved (Table 2). The C—O bond lengths in the protonated carboxyl group (COOH) are similar to the values found in other non-ionized carboxyl groups (Allen *et al.*, 1987).

In the crystal of (I), the C4—C8 chain of the glutarate ion is almost planar; the average deviation of these C atoms from the weighted least-squares plane through them is 0.026 Å. The orientation of the carboxyl COO$^-$ and COOH groups with respect to the carbon chain is described by the O1—C4—C5—C6 [12.6 (2)°] and O3—C8—C7—C6 [127.3 (2)°] torsion angles. The optimized geometry of the glutarate anion is illustrated in Fig. 1(*b*). Both C—O bonds of the ionized carboxyl group are slightly shorter than in the crystal. In the COOH group, the double C═O bond is shorter and the single C—OH bond is longer in the optimized glutarate anion than in the crystal. This is likely to be due to the hydrogen-bond interactions present in the crystal. The ionized carboxyl group (COO$^-$) in the optimized glutarate ion, in contrast with the crystal, is coplanar with the chain of C atoms, with an O1—C4—C5—C6 torsion angle of 0.7°, while the O3—C8—C7—C6 torsion angle, describing the rotation of the COOH group, is 107.4°. The differences between the orientation of the COO$^-$ and COOH groups in relation to the plane of the C atoms between the X-ray geometry and the optimized gas-phase calculations are due to the mutual arrangement of the oppositely charged units that form the hydrogen-bonding system (Fig. 3*a*), since the calculations were performed on the isolated glutarate ion.

The water molecule is involved in three hydrogen bonds, in two as donor and in one as acceptor. As donor, the water molecule forms O—H···O hydrogen bonds with two glutarate anions, whereas as acceptor, it forms hydrogen bonds with the melaminium residue *via* the H atom of an amine group.

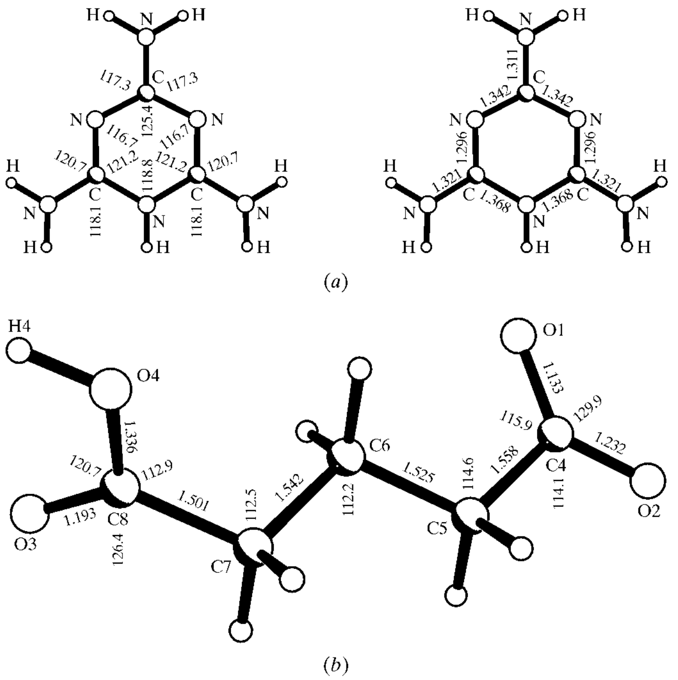

Figure 1
The results of the optimized gas-phase calculations (*a*) for the melaminium cation and (*b*) for the glutarate anion. Bond lengths are given in Å and angles in °.

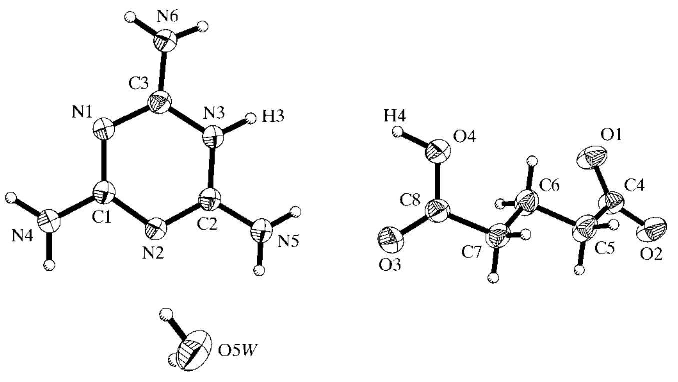

Figure 2
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

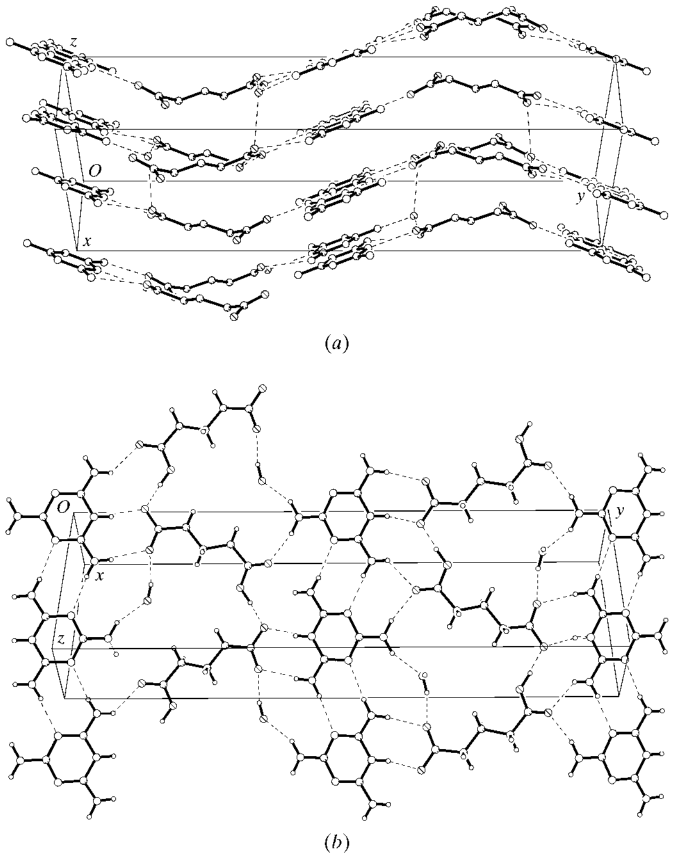

Figure 3
(*a*) The crystal packing in (I), showing the stacking structure. Dashed lines represent hydrogen bonds and H atoms have been omitted for clarity. (*b*) The layer of hydrogen-bonded melaminium and glutarate ions and water molecules parallel to the *b* axis.

In the crystal of (I), the melaminium residues interconnected by N—H···N hydrogen bonds form complementary joined positively charged chains that form a stacking structure. Within one stack, the melaminium residues are separated by ~3.27 Å. This distance is shorter than that between π-aromatic ring systems (~3.4 Å; Pauling, 1960) and indicates a π–π interaction between the melaminium rings within the stack. The glutarate anions form hydrogen-bonded polymeric zigzag chains, $[\cdots HOOC(CH_2)_3COO\cdots HOOC(CH_2)_3COO\cdots]_n$, that interconnect neighbouring melaminium chains to form a layer (Fig. 3*b*) located in the crystal along the [010] direction (Fig. 3*a*) and which is inclined by ~46 and ~44° to the *a* and *c* axes, respectively. The water molecules connect neighbouring layers *via* hydrogen bonds that stabilize the stacking structure.

Experimental

Melamine was dissolved in a 20% solution of glutaric acid and the resulting solution was evaporated slowly. After several days, colourless crystals of (I) appeared.

Crystal data

$C_3H_7N_6^+\cdot C_5H_7O_4^-\cdot H_2O$
$M_r = 276.27$
Monoclinic, $P2_1/c$
$a = 4.5390$ (10) Å
$b = 28.544$ (6) Å
$c = 9.863$ (2) Å
$\beta = 97.57$ (3)°
$V = 1266.7$ (5) Å^3
$Z = 4$
$D_x = 1.449$ Mg m^{-3}
$D_m = 1.444$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
Cell parameters from 1600 reflections
$\theta = 3$–28°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colourless
0.20 × 0.18 × 0.12 mm

Data collection

Kuma KM-4 diffractometer with a CCD area-detector
ω scans
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min} = 0.976$, $T_{\max} = 0.985$
11 010 measured reflections
2920 independent reflections
1605 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 28°$
$h = -5 \rightarrow 5$
$k = -37 \rightarrow 37$
$l = -12 \rightarrow 13$

Table 1
Selected geometric parameters (Å, °).

N1—C3	1.327 (2)	O1—C4	1.254 (2)
N1—C1	1.356 (2)	O2—C4	1.266 (2)
N2—C2	1.326 (2)	O3—C8	1.210 (2)
N2—C1	1.356 (2)	O4—C8	1.310 (2)
N3—C2	1.354 (2)	C4—C5	1.497 (2)
N3—C3	1.367 (2)	C5—C6	1.508 (2)
C1—N4	1.318 (2)	C6—C7	1.520 (2)
C2—N5	1.321 (2)	C7—C8	1.490 (2)
C3—N6	1.321 (2)		
C3—N1—C1	115.9 (1)	O2—C4—C5	117.8 (1)
C2—N2—C1	116.0 (1)	C4—C5—C6	116.3 (1)
C2—N3—C3	119.6 (1)	C5—C6—C7	112.1 (1)
N1—C1—N2	125.6 (1)	C8—C7—C6	112.9 (1)
N2—C2—N3	121.6 (1)	O3—C8—O4	121.3 (1)
N1—C3—N3	121.4 (1)	O3—C8—C7	125.1 (1)
O1—C4—O2	122.2 (1)	O4—C8—C7	113.6 (1)
O1—C4—C5	120.1 (1)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2$^{\rm i}$	0.91 (2)	1.83 (2)	2.728 (2)	168 (1)
N4—H41···O5$W^{\rm ii}$	0.95 (2)	2.01 (2)	2.895 (2)	155 (1)
N4—H42···O3$^{\rm iii}$	0.94 (2)	2.07 (2)	2.991 (2)	166 (1)
N5—H51···N2$^{\rm iii}$	0.87 (2)	2.13 (2)	2.991 (2)	173 (1)
N5—H52···O3	0.85 (2)	2.18 (2)	2.850 (2)	135 (1)
N6—H61···N1$^{\rm iv}$	0.91 (2)	2.17 (2)	3.074 (2)	171 (1)
N6—H62···O1$^{\rm i}$	0.87 (2)	2.05 (2)	2.903 (2)	167 (1)
O4—H4···O2$^{\rm i}$	0.99 (2)	1.62 (2)	2.597 (2)	173 (2)
O5W—H5W1···O1$^{\rm v}$	0.89 (2)	1.89 (2)	2.764 (2)	165 (2)
O5W—H5W2···O1$^{\rm vi}$	0.92 (2)	1.97 (2)	2.891 (2)	174 (2)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.070$
$S = 1.01$
2920 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0084 (10)

All H atoms were refined, except those of the CH_2 groups, which were constrained as riding, with C—H distances of 0.97 Å.

Data collection: *KM*-4 *CCD Software* (Kuma Diffraction, 2000); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; 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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1570). Services for accessing these data are described at the back of the journal.

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