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Melaminium acetate acetic acid solvate monohydrate

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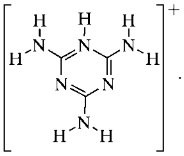
The crystals of the title new melaminium salt, 2,4,6-triamino-1,3,5-triazin-1-ium acetate acetic acid solvate monohydrate, $C_3H_7N_6^+ \cdot CH_3COO^- \cdot CH_3COOH \cdot H_2O$, are built up from singly protonated melaminium residues, acetate anions, and acetic acid and water molecules. The melaminium residues are interconnected by N—H···N hydrogen bonds to form chains along the [010] direction. These chains of melaminium residues form stacks aligned along the *a* axis. The acetic acid molecules interact with the acetate anions *via* the H atom of their carboxylic acid groups and, together with the water molecules, form layers that are parallel to the (001) plane. The oppositely charged moieties interact *via* multiple N—H···O hydrogen bonds that stabilize a pseudo-two-dimensional stacking structure.

Comment

This study forms part of our investigation of the characterization of the hydrogen bonds formed by the melamine molecule in the solid state (Janczak & Perpétuo, 2001*a*,*b*,*c*,*d*). The melamine molecule and its organic and inorganic complexes or salts can, *via* multiple hydrogen bonds, develop supramolecular structures 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 different hydrogen-bonding systems, we have studied the solid-state structure of singly protonated melaminium acetate acetic acid solvate monohydrate, (I), and the results are presented here.

The asymmetric unit of (I) consists of two molecules, namely two melaminium residues protonated at one ring N atom, two acetate anions, two acetic acid molecules and two water molecules (Fig. 1). The two independent melaminium cations do not differ significantly, but the six-membered aromatic rings exhibit significant distortion from the ideal hexagonal form. The internal C—N—C angle at the protonated N atom (N2/N8) is significantly greater than the other two ring C—N—C angles (Table 1). 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 atom N2/N8, the internal N—C—N angle containing only non-protonated N atoms is significantly greater than either of the N—C—N angles containing both protonated and non-protonated N atoms. This correlation between the internal C—N—C angles within the melaminium rings is quite 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*) and bis(melaminium) sulfate dihydrate (Janczak & Perpétuo, 2001*d*), *i.e.* those singly protonated melaminium salts that have been structurally characterized to date.



$\cdot CH_3COO^- \cdot CH_3COOH \cdot H_2O$

(I)

The melaminium residues in the crystal of (I) are involved in nine hydrogen bonds, in seven of them as donor H and in the remaining two as acceptor H. The four N—H···N bonds link the melaminium residue with two neighbouring melaminium residues to form a chain (Fig. 2), while the five N—H···O bonds link a melaminium residue with two acetate ions, two acetic acid molecules and one water molecule. The N—H···N hydrogen bonds are much more linear than the N—H···O bonds.

The geometries of the two independent acetate ions do not differ significantly. The C—O bond lengths in the acetate moieties indicate delocalization of the charge on both O atoms, since the C—O bond lengths are intermediate between single Csp^2—O and double Csp^2=O, and correlate well with values for carboxylate anions (1.247–1.262 Å; Allen *et al.*, 1987). One of the two independent acetate ions is involved as acceptor in four hydrogen bonds (O11 and O12), while the other acetate ion is involved in five hydrogen bonds.

Both independent acetic acid molecules exhibit similar geometry. The OH group of the COOH in both acetic acid molecules joins the acetate ions *via* O—H···O hydrogen bonds. The carbonyl O atom of COOH groups acts as acceptor in hydrogen bonds with the amine groups of two different melaminium residues. The slight differences in C—O distances for equivalent bonds in the acetate ions, as well as in the acetic acid molecules, correlate with the number and strength of the hydrogen bonds in which the O atoms are involved (Table 2).

The water molecules form a hydrogen-bonded dimeric structure (O1*W*—H2*W*1···O2*W*), with an O···O distance of

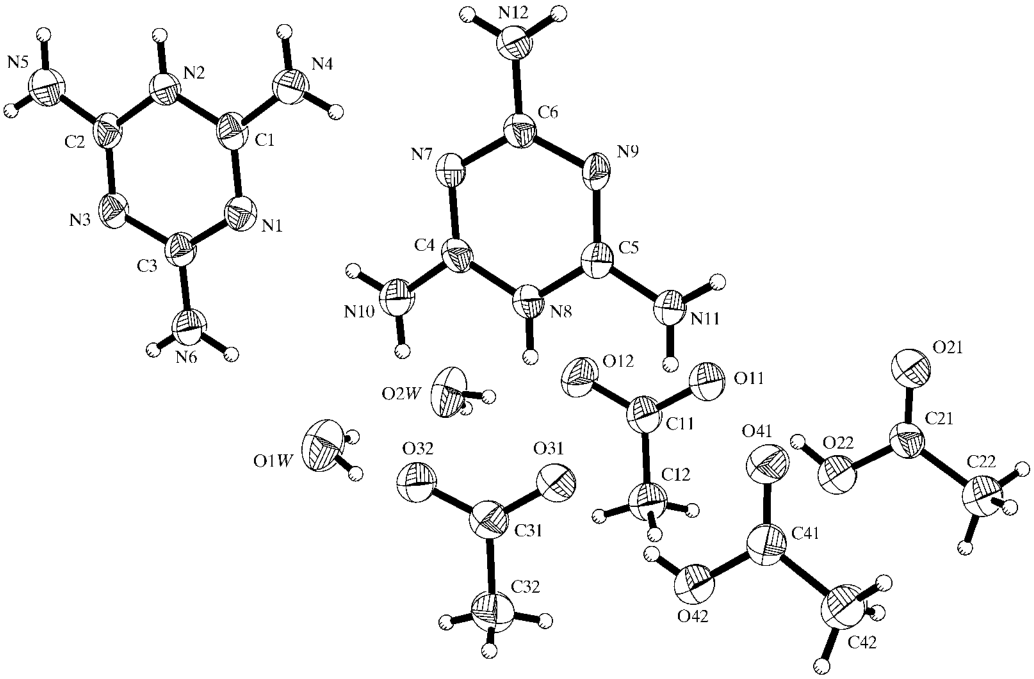


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.

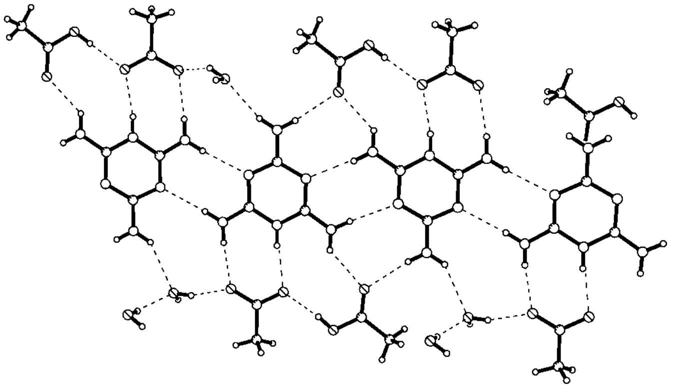


Figure 2
An [010] projection of the packing in (I) showing an N—H···N-interconnected melaminium chain, which interacts *via* N—H···O hydrogen bonds with the acetate anions and acetic acid and water molecules.

2.853 (3) Å, joining the hydrogen-bonded acetic acid–acetate moieties. The first water molecule (O1*W*) is involved in three hydrogen bonds, in two of which it acts as donor H, with O2*W* of a water molecule and O32 of an acetate ion, and in the other as acceptor H, with the amine group of a melaminium residue. The second water molecule is involved in four hydrogen bonds, with two acetate ions, a water molecule and an amine group of a melaminium residue. Full details of the hydrogen-bonding geometry are given in Table 2.

In the crystal of (I), the melaminium residues form complementary planar positively charged chains interconnected by N—H···N hydrogen bonds, and these chains form stacks parallel to the (001) plane (Fig. 3). Within one stack, the melaminium residues are separated by ~3.25 Å. This is slightly shorter than the distance between π-aromatic ring systems (~3.4 Å; Pauling, 1960) and indicates π–π interaction between the melaminium rings. The hydrogen-bonded acetic acid–acetate moieties are interconnected by the dimeric structure of the hydrogen-bonded water, forming negatively charged layers that are located parallel to the (001) plane. These oppositely charged moieties are extensively interconnected by multiple hydrogen bonds to form columnar supramolecular aggregates which are aligned along the *a* axis.

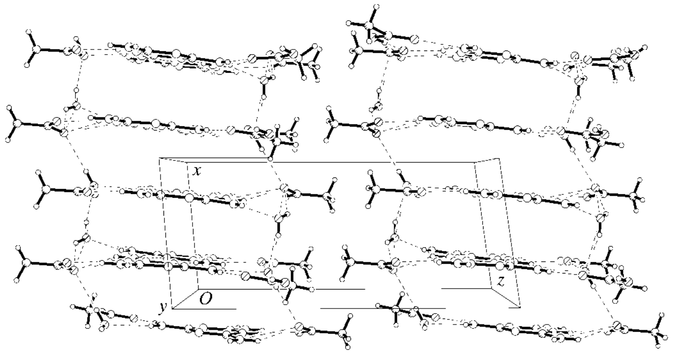


Figure 3
A view of the molecular arrangement in the unit cell of (I), showing the hydrogen-bonding interactions (dashed lines).

Experimental

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

Table 1
Selected geometric parameters (Å, °).

O11—C11	1.264 (2)	O31—C31	1.252 (2)
O12—C11	1.250 (2)	O32—C31	1.266 (2)
C12—C11	1.478 (3)	C32—C31	1.493 (3)
O21—C21	1.208 (2)	O41—C41	1.209 (2)
O22—C21	1.317 (2)	O42—C41	1.320 (3)
C21—C22	1.483 (3)	C41—C42	1.481 (3)
C1—N1—C3	116.4 (2)	C4—N7—C6	116.1 (2)
N1—C1—N2	120.8 (2)	N7—C4—N8	121.3 (2)
C2—N2—C1	119.9 (2)	C5—N8—C4	119.8 (2)
N3—C2—N2	121.8 (2)	N9—C5—N8	121.7 (2)
C2—N3—C3	116.0 (2)	C5—N9—C6	115.3 (2)
N1—C3—N3	125.0 (2)	N9—C6—N7	125.8 (2)

Crystal data

$C_3H_7N_6^+ \cdot C_2H_3O_2^- \cdot C_2H_4O_2 \cdot H_2O$
M_r = 264.26
Triclinic, $P\overline{1}$
a = 6.8590 (10) Å
b = 12.427 (2) Å
c = 15.307 (3) Å
α = 92.31 (3)°
β = 95.87 (3)°
γ = 103.36 (3)°
V = 1260.0 (4) Å^3
Z = 4
D_x = 1.393 Mg m^{-3}
D_m = 1.39 Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
Cell parameters from 69 reflections
θ = 9–16°
μ = 0.12 mm^{-1}
T = 293 (2) K
Parallelepiped, colourless
0.33 × 0.18 × 0.15 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min}$ = 0.962, $T_{\max}$ = 0.983
7979 measured reflections
4252 independent reflections
2141 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 25.1°
$h = -8 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$
2 standard reflections every 50 reflections intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.057
S = 1.00
4252 reflections
347 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0120P)^2 + 0.0133P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\min}$ = −0.14 e Å^{-3}

H atoms bonded to C and N atoms were treated as riding, with C—H = 0.96 and N—H = 0.86 Å. The coordinates of the H atoms bonded to O atoms were refined, and the resulting range of O—H distances was 0.80 (2)–0.83 (2) Å.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O11$^{\rm i}$	0.86	1.93	2.773 (2)	168
N4—H4*NA*···N7	0.86	2.14	3.002 (2)	176
N4—H4*NB*···O12$^{\rm i}$	0.86	1.93	2.772 (2)	166
N5—H5*NA*···N9$^{\rm ii}$	0.86	2.14	3.002 (2)	176
N5—H5*NB*···O21$^{\rm i}$	0.86	2.12	2.782 (2)	133
N6—H6*NA*···O1*W*	0.86	2.13	2.936 (2)	157
N6—H6*NB*···O41$^{\rm ii}$	0.86	2.13	2.981 (2)	173
N8—H8···O31	0.86	1.97	2.817 (2)	167
N10—H10N···N1	0.86	2.15	3.008 (2)	176
N10—H11N···O32	0.86	2.12	2.916 (2)	155
N11—H12N···N3$^{\rm iii}$	0.86	2.13	2.982 (2)	175
N11—H13N···O41	0.86	2.08	2.746 (2)	134
N12—H14N···O21$^{\rm iv}$	0.86	2.18	3.040 (2)	174
N12—H15N···O2*W*$^{\rm i}$	0.86	2.33	3.085 (2)	146
O22—H222···O11	0.83 (2)	1.76 (2)	2.581 (2)	171 (3)
O42—H421···O31	0.79 (3)	1.85 (2)	2.622 (2)	167 (3)
O1*W*—H1*W*1···O32	0.82 (2)	2.16 (2)	2.844 (2)	141 (3)
O1*W*—H2*W*1···O2*W*	0.80 (2)	2.10 (2)	2.853 (2)	158 (3)
O2*W*—H1*W*2···O12	0.82 (2)	1.86 (2)	2.667 (2)	165 (3)
O2*W*—H2*W*2···O32$^{\rm v}$	0.80 (2)	2.20 (2)	2.993 (2)	177 (3)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1181). Services for accessing these data are described at the back of the journal.

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