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Melaminium formate

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Crystals of a new melaminium salt, 2,4,6-triamino-1,3,5-triazin-1-ium formate, $C_3H_7N_6^+\cdot CHO_2^-$, consist of singly protonated melaminium residues and formate anions. The components are linked by hydrogen bonds into a three-dimensional framework structure. The melaminium residues are interconnected by two pairs of N—H···N hydrogen bonds into chains in the form of stacks, with a distance of 3.34 (1) Å between the triazine rings, clearly indicating *π*–*π* interactions. The chains of melaminium residues are interconnected *via* N—H···O hydrogen bonds by the formate anions, forming a non-covalent superstructure.

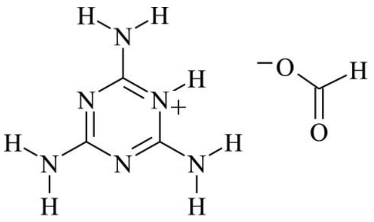
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(O–C) = 0.001 Å
R factor = 0.036
wR factor = 0.096
Data-to-parameter ratio = 16.9

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

Comment

Melamine and its derivatives and inorganic or organic salts can develop well defined non-covalent supramolecular nanoarchitectures *via* multiple hydrogen bonds by self-assembly of components containing complementary arrays of hydrogen-bonding sites (Desiraju, 1990; MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Janczak & Perpétuo, 2001; Sherington & Taskinen, 2001). In order to expand the understanding of the solid-state physical-organic chemistry of compounds containing multiple N—H···N and N—H···O hydrogen-bonding systems, we present here the solid-state structure of melaminium formate, (I). The asymmetric unit of (I) consists of a melaminium cation, singly protonated at a ring N atom, and the formate anion (Fig. 1). Selected geometric parameters are given in Table 1.



(I)

The amine groups (NH_2) are almost coplanar with the six-membered aromatic triazine ring [the N atoms of the NH_2 groups are displaced from the plane by 0.040 (1)–0.059 (1) Å]. The triazine ring is planar, but it exhibits significant distortions from the ideal hexagonal form as reported for other melaminium salts (Janczak & Perpétuo, 2002, 2003). Protonation of the ring also disturbs the C—N bonds within the ring when compared with the neutral melamine crystal structure (Varghese *et al.*, 1977). The C—N bonds involving the protonated N atom are slightly longer than the others within the

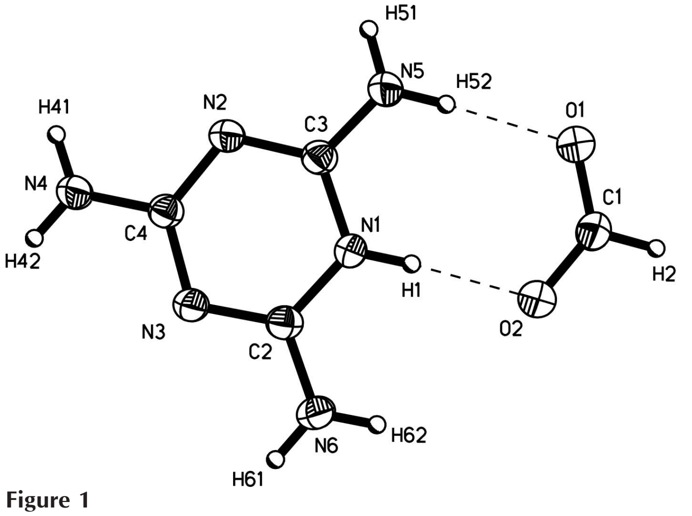


Figure 1
A view of the asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.

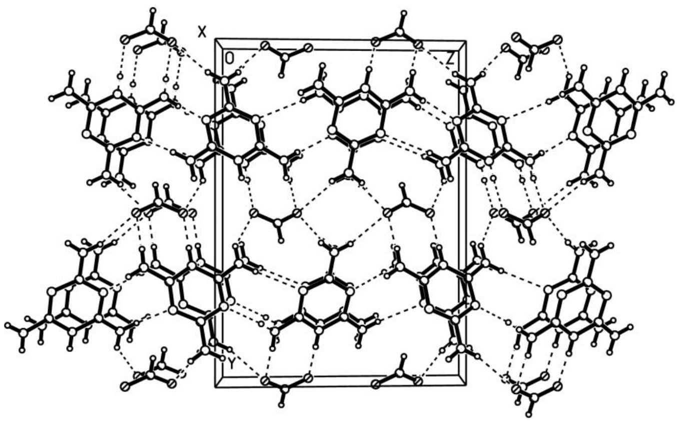


Figure 2
A view of the crystal packing in (I), showing the hydrogen-bonded N—H···N chains that form the π–π stacks (along the [100] direction). Hydrogen bonds are drawn as dashed lines.

ring. Thus there is overwhelming evidence for a partially localized double bond form, *i.e.* the bond order of the N2—C3 and C2—N3 bonds is greater than the other C—N intra-ring bonds. The *ab initio* molecular orbital calculations performed for the neutral melamine molecule reveal D_{3h} symmetry with C—N distances of 1.325 Å within the ring (Drozd & Marchewka, 2005), while corresponding calculations for the singly protonated melaminium cation predict C_{2v} symmetry (Janczak & Perpétuo, 2004). These calculations support the conclusion concerning the partial localization of the double-bond form. Additionally, protonation of the triazine ring of melamine leads to shortening of the C—NH_2 bonds in relation to the non-protonated melamine molecule in the solid state (Varghese *et al.*, 1977), as well as in the gas phase (Drozd & Marchewka, 2005). These variations are supported by *ab initio* calculations, as reported previously (Janczak & Perpétuo, 2002, 2003, 2004).

A search of the Cambridge Structural Database (Version 5.26; Allen, 2002) for systems containing a singly protonated melaminium residue yields 23 structures, all of which show melaminium ring distortions quite similar to those found here. The formate anion is planar. The C—O bond lengths (Table 1) are 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 carboxyl group. The C—O distances and O—C—O angle in the formate ion correlate well with those obtained by *ab initio* molecular orbital calculations (C1—O1 = 1.232 Å, C1—O2 = 1.250 Å and O—C—O = 126.5°; Frisch *et al.*, 1998).

An extensive set of hydrogen bonds (Table 2) links the independent components of (I) into a continuous framework superstructure. Each melaminium residue is involved in nine hydrogen bonds. In seven of these it acts as a donor and as an acceptor in the remaining two. Two pairs of N—H···N hydrogen bonds link pairs of melaminium cations, related to one another by a combination of *n*-glide plane and 2_1 screw axis and, together with translation, these form stacked chains parallel to [100] (Fig. 2). In these hydrogen-bonded chains, the alternate triazine rings are not parallel but are inclined at 42.5 (1)° to each other. This chain formation is different from that found in the other singly protonated melaminium crystal structures (Allen, 2002), in which the melaninium residues form planar linear chains. In the present case, the triazine rings within each stack are separated by 3.34 (1) Å. This distance is slightly shorter than that for a π-aromatic ring system (3.4 Å; Pauling, 1960) and indicates strong π–π interactions between the triazine rings within the stack. Five N—H···O hydrogen bonds link each melaminium cation to four formate anions (Table 2).

The formate $HCOO^-$ anions interconnect the neighbouring stacks of melaminium chains into a three-dimensional non-covalent bonded superstructure. Atom O1 of the formate anion is involved as an acceptor in hydrogen bonds with three melaminium residues, while the other O atom (O2) acts as an acceptor in hydrogen bonds with two melaminium cations that are related by an inversion centre and translation.

Experimental

Melamine (99%) was dissolved in hot 10% formic acid (>98%) and the resulting solution cooled to room temperature. After several days, colourless single crystals of (I) had formed.

Crystal data

$C_3H_7N_6^+\cdot CHO_2^-$
M_r = 172.16
Monoclinic, $P2_1/n$
a = 3.957 (1) Å
b = 15.798 (3) Å
c = 11.461 (2) Å
β = 94.14 (1)°
V = 714.6 (3) Å^3
Z = 4
D_x = 1.600 Mg m^{-3}
D_m = 1.60 (1) Mg m^{-3}
D_m measured by flotation in chloroform/bromoform
Mo $K\alpha$ radiation
Cell parameters from 1252 reflections
θ = 3.1–29.5°
μ = 0.13 mm^{-1}
T = 295 (2) K
Parallelepiped, colourless
0.36 × 0.20 × 0.12 mm

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Data collection

Kuma KM-4 diffractometer with CCD area-detector
ω scans
Absorption correction: analytical [face-indexed; *SHELXTL* (Sheldrick, 1990)]
$T_{\min} = 0.950$, $T_{\max} = 0.984$
8423 measured reflections
1840 independent reflections
1300 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 29.5°$
$h = -5 \rightarrow 4$
$k = -21 \rightarrow 21$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.01$
1840 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2448 (12)	N3—C2	1.3241 (13)
O2—C1	1.2416 (12)	N3—C4	1.3560 (12)
N1—C2	1.3550 (12)	N4—C4	1.3224 (13)
N1—C3	1.3670 (12)	N5—C3	1.3120 (12)
N2—C3	1.3283 (13)	N6—C2	1.3225 (13)
N2—C4	1.3522 (12)		
O2—C1—O1	128.16 (10)	N3—C2—N1	122.01 (9)
C2—N1—C3	118.90 (9)	N2—C3—N1	121.75 (9)
C3—N2—C4	115.84 (9)	N2—C4—N3	125.42 (10)
C2—N3—C4	116.00 (8)		

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	0.86	1.86	2.7100 (12)	170
N5—H52$\cdots$O1	0.86	1.94	2.7863 (13)	167
N4—H41$\cdots$O1$^{\rm i}$	0.86	2.05	2.8959 (12)	169
N4—H42$\cdots$O1$^{\rm ii}$	0.86	2.27	3.0593 (12)	153
N5—H51$\cdots$N3$^{\rm iii}$	0.86	2.09	2.9408 (13)	173
N6—H61$\cdots$N2$^{\rm iv}$	0.86	2.38	3.2191 (14)	165
N6—H62$\cdots$O2$^{\rm v}$	0.86	2.26	2.9690 (13)	140

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

H atoms were treated as riding, with N—H distances of 0.86 Å, C—H distances of 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ of the parent N or C atoms.

Data collection: *KM-4 CCD Software* (Kuma, 2001); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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