Cocrystallization of melaminium levulinate monohydrate

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Crystals of 2,4,6-triamino-1,3,5-triazin-1-ium levulinate (4-oxo-pentanoate) monohydrate, $C_3H_7N_6^+ \cdot C_5H_7O_3^- \cdot H_2O$, are formed via self-assembled hydrogen bonding by cocrystallization of melamine and levulinic acid. Two N—H···N hydrogen bonds and four N—H···O hydrogen bonds connect two melaminium entities such that each of two pairs of N—H···O bonds bridges two H atoms belonging to the amine groups of two different melaminium cations via the carbonyl O atom of one levulinate molecule.

Comment

One of the primary objectives of crystal engineering is the construction of self-assembled hydrogen-bonded molecular materials (Desiraju, 1996; Philip & Stoddart, 1996). Currently, many research groups are involved in synthesizing one-, two- and three-dimensional clustered self-assembled hydrogen-bonding superlattice structures (Zerkowski et al., 1990; Whitesides et al., 1991; Ghadiri et al., 1993; Mathias, Simanek & Whitesides, 1994; Mathias, Simanek, Zerkowski et al., 1994; Kimizuka et al., 1995; Lange et al., 1997), while others are synthesizing metal-ion-incorporated systems (Goddgame et al., 1999; Zhang et al., 1999). Various studies have been carried out using melamine and its derivatives as versatile components, because the presence of amino groups in these compounds means that they can easily form several types of self-organized superlattices with suitable hydrogen-bonding donor and acceptor molecules (Janczak & Perpétuo, 2001a,b,c,d; Perpétuo & Janczak, 2002). The combination of levulinic acid with melamine leads to the formation of a 1:1 adduct, namely 2,4,6-triamino-1,3,5-triazin-1-ium levulinate monohydrate, $C_3H_7N_6^+ \cdot C_5H_7O_3^- \cdot H_2O$, (I), the crystal structure of which is reported here.

The asymmetric unit of (I) consists of two oppositely charged ions, viz. a protonated melaminium ion and a levulinate ion, and one water molecule (Fig. 1). Two melaminium

entities are connected to one another via two N6—H···N3 hydrogen bonds, two N5—H···O3 hydrogen bonds and two N6—H···O3 hydrogen bonds; specifically, the four N—H···O interactions bridge four amine H atoms belonging to two different melaminium entities via the carbonyl O atoms of two levulinate ions. In addition, two N4—H···O1W and two O1W—H···O1 hydrogen bonds link the two cations and two anions. The bridging water molecules and the bridging carbonyl O atoms between the melaminium and levulinate entities form large pores (0L and 0R in Fig. 1). Finally, two water molecules, O1W[ii] and O1W[iii], are involved in bridging melaminium and levulinate entities in the next row along the b axis [symmetry codes: (ii) $-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (iii) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$]. There are hydrogen bonds between water molecules and the O1 atoms of the levulinate anions (Table 2).

(I)
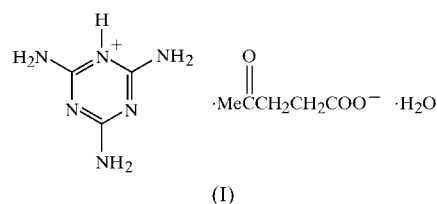
The six-membered aromatic ring of the melaminium ion exhibits slight distortions from the ideal hexagonal form (Janczak & Perpétuo, 2001c) and from the structure of neutral melamine (Hughes, 1941). The C2—N2—C1 angle (Table 1) at the protonated N atom of the melaminium entity is 4° larger than the C1—N1—C3 angle at a non-protonated N atom. Also, the N1—C3—N3 angle, involving the non-protonated ring N atoms, is about 5° larger than the N3—C2—N2 angle, involving protonated and non-protonated N atoms. The contraction of the C1—N1—C3 and C2—N3—C3 angles from 120 to ~115° appears to be correlated with expansion of the
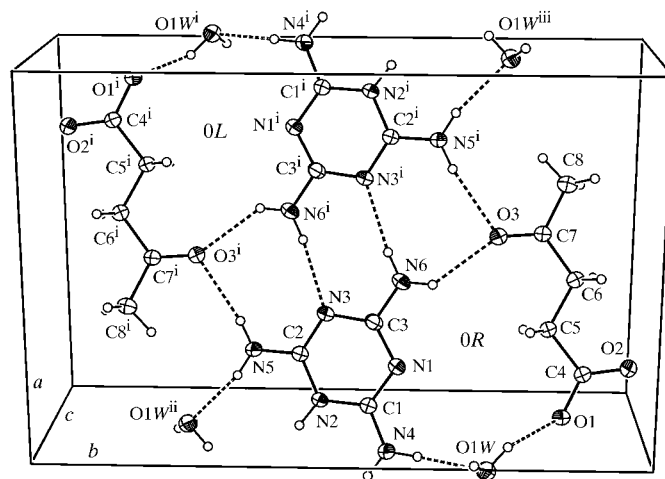

Figure 1
The molecular structure and unit-cell contents of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. Pores formed by hydrogen bonds between melaminium cations and levulinate anions are designated 0L and 0R. [Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) $-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (iii) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.]

organic compounds

N1—C3—N3 angle to ~127°, while the N1—C1—N2 and N3—C2—N2 angles are both close to ideal, as is the C2—N2—C1 angle. On the other hand, the C2—N2—C1 and C1—N1—C3 angles are 3° larger than the equivalent angle (116°) in neutral melamine (Hughes, 1941). The N1—C3—N3 and N3—C2—N2 angles are similar to those in neutral melamine.

Experimental

An aqueous solution (50 ml) of levulinic acid (0.22 g, 2 mmol) was added to melamine (0.26 g, 2 mmol) dissolved in hot water (100 ml). The resulting solution was cooled slowly to ambient temperature and filtered. Colorless crystals of (I) appeared after the solution had been left to stand for several days in the presence of air at room temperature.

Crystal data

$C_3H_7N_6^+ \cdot C_5H_7O_3^- \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 260.27$	Cell parameters from 23
Monoclinic, $P2_1/c$	reflections
$a = 10.538 (2)$ Å	$\theta = 11.3$–$13.9°$
$b = 16.214 (3)$ Å	$\mu = 0.11$ mm^{-1}
$c = 7.1988 (14)$ Å	$T = 293 (2)$ K
$\beta = 95.85 (3)°$	Block, colorless
$V = 1223.6 (4)$ Å^3	$0.46 \times 0.43 \times 0.36$ mm
$Z = 4$	
$D_x = 1.413$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$h = -13 \rightarrow 13$
Non-profiled $\omega/2\theta$ scans	$k = -21 \rightarrow 21$
5931 measured reflections	$l = 0 \rightarrow 9$
2806 independent reflections	3 standard reflections
1899 reflections with $I > 2\sigma(I)$	every 400 reflections
$R_{int} = 0.030$	intensity decay: 1%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 0.3261P]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2806 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
175 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.277 (2)	N2—C1	1.372 (2)
O2—C4	1.224 (2)	N3—C2	1.325 (2)
O3—C7	1.208 (2)	N3—C3	1.355 (2)
N1—C1	1.328 (2)	N4—C1	1.312 (2)
N1—C3	1.337 (2)	C4—C5	1.515 (2)
N2—C2	1.351 (2)		
C1—N1—C3	115.18 (16)	N1—C3—N3	127.00 (16)
C2—N2—C1	119.03 (15)	O2—C4—O1	123.83 (17)
C2—N3—C3	115.05 (15)	O2—C4—C5	119.90 (16)
N1—C1—N2	121.66 (16)	O1—C4—C5	116.27 (16)
N3—C2—N2	122.03 (17)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O1^{iv}	0.89 (2)	1.80 (2)	2.689 (2)	179 (2)
O1W—H1$W\cdots$O1	0.86 (3)	1.90 (3)	2.697 (2)	154 (3)
O1W—H2$W\cdots$O1^v	0.85 (3)	1.99 (3)	2.825 (2)	168 (3)

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

H atoms on atoms N2 and O1W were located in a difference map and their parameters were refined isotropically. All other H atoms were positioned geometrically and constrained to ride on their parent atoms, with U_{iso}(H) values of $1.2U_{eq}$(C,N) (CH$_2$ and NH$_2$ H atoms) or $1.5U_{eq}$(C) (CH$_3$ H atoms).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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