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# An orthorhombic polymorph of melaminium chloride hemihydrate

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Crystals of an orthorhombic polymorph of 2,4,6-triamino-1,3,5-triazin-1-ium chloride hemihydrate, $C_3H_7N_6^+\cdot Cl^-\cdot 0.5H_2O$, were obtained by cocrystallization experiments under aqueous acidic conditions (HCl, pH = 2). In the crystal structure, the melaminium ions, chloride anions and water molecules are linked *via* hydrogen bonds. All H atoms of the melaminium cation are involved in hydrogen bonds. The chloride anions and the water molecules lie on mirror planes. In the *c* direction, the melaminium ions are stacked by $\pi$–$\pi$ interactions.

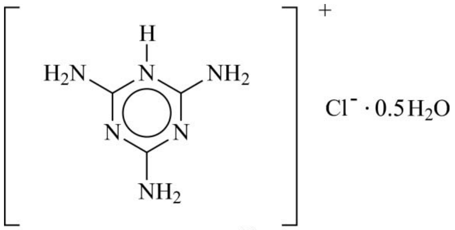
**Key indicators**

Single-crystal X-ray study
$T$ = 210 K
Mean $\sigma$(N–C) = 0.003 Å
$R$ factor = 0.030
$wR$ factor = 0.063
Data-to-parameter ratio = 12.5

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

## Comment

The title compound, (I), was obtained during cocrystallization studies of guanidinium chloride in $H_2O$/HCl (pH=2).



(I)

The formation of this substance was already described (Hughes, 1941). No structural information is given because only poor diffraction signals could be obtained. However, the needle-like crystals were found to be orthorhombic with $a$ = 16.75 Å, $b$ = 12.29 Å, $c$ = 6.93 Å, space group *Cmcm*, *Cmc*$2_1$ or *C*2*cm* (Hughes, 1941). The investigation was not pursued any further.

A monoclinic polymorph of melaminium chloride hemihydrate was reported (Janczak & Perpétuo, 2001*c*) with two half-melaminium ions in the asymmetric unit. The two residues do not differ significantly from one another.

The asymmetric unit of (I) consists of a melaminium ion, two half-chloride anions and half a water molecule (Fig. 1). The Cl anions and the water molecule lie on a mirror plane.

The C—N—C angle at the protonated N atom is greater than the other two C—N—C angles (Table 1). These differences were also reported for the monoclinic polymorph (Janczak & Perpétuo, 2001*c*) and anhydrous melaminium chloride (Jing *et al.*, 2003), as well as for other singly protonated melaminium salts [bromide (Scoponi *et al.*, 1992), phthalate (Janczak & Perpétuo, 2001*a*), terephthalate (Zhang *et al.*, 2004)] and for multiply protonated melaminium salts [diperchlorate (Martin & Pinkerton, 1995) 4-hydroxybenzenesulfonate (Janczak & Perpétuo, 2001*b*), trichloride,

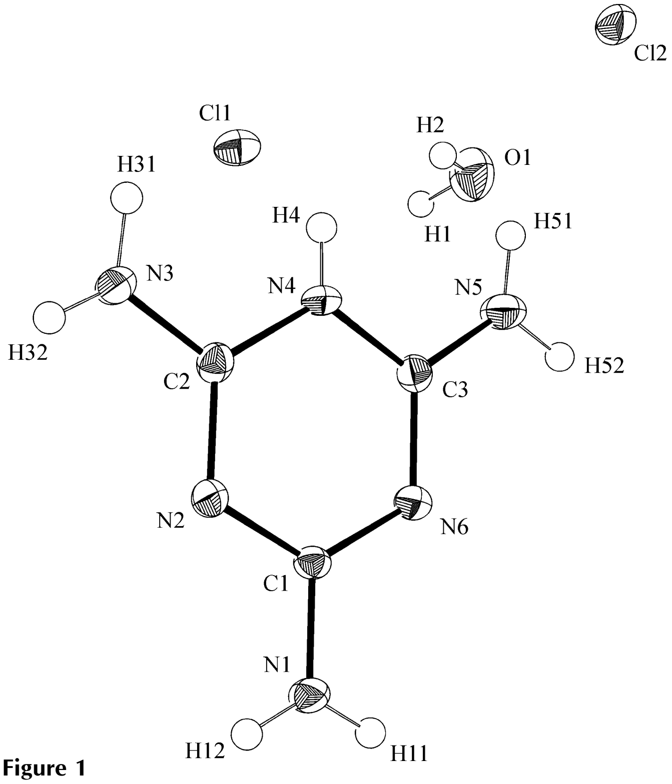


**Figure 1**
The asymmetric unit of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

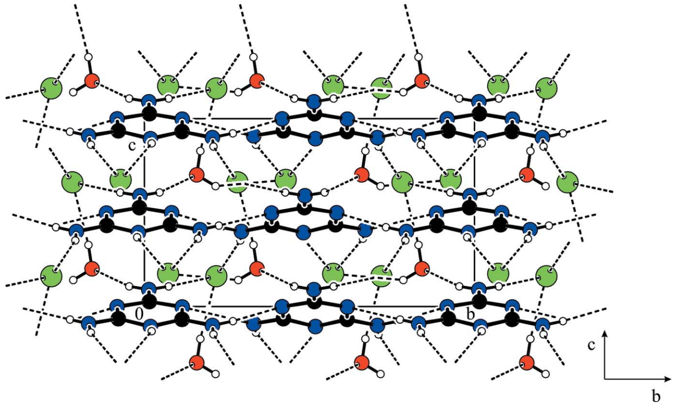


**Figure 2**
Packing diagram of the title compound with a view down the *a* axis. Hydrogen bonds are shown as dashed lines.

cocrystallized with cyanuric acid (Wang *et al.*, 1990)]. Zhang & Chen (2005) reported an extensive hydrogen bonding system in melaminium salts with aromatic carboxylates.

The crystal structure is stabilized by hydrogen bonds and $\pi$–$\pi$ stacking interactions. The melaminium ions are linked by N—H$\cdots$N hydrogen bonds, forming chains along *b* (Fig. 2). The chains are interconnected by N—H$\cdots$Cl and N—H$\cdots$O hydrogen bonds. The Cl and O acceptor atoms are located in planes at $x = 0$ and $x = \frac{1}{2}$. In addition, the melaminium residues are stacked in the *c* direction by $\pi$–$\pi$ interactions with a distance of 3.49 Å between the melaminium cations, which is typical for $\pi$–$\pi$ stacking between aromatic ring systems (symmetry code: $x, -y+1, z+\frac{1}{2}$). Details of the hydrogen-bond network are listed in Table 2.

## Experimental

Guanidine hydrochloride (2.87 g, 30 mmol) and sodium methoxide (1.62 g, 30 mmol) were added to dried methanol (20 ml). The mixture was refluxed continually at 415 K until the solution became yellow–brown. The mixture was stored for a week at 277 K under acidic conditions ($H_2O$/HCl pH=2). A yellow crude precipitate was formed and recrystallized from methanol to afford colourless prismatic crystals suitable for X-ray analysis.

### *Crystal data*

$C_3H_7N_6^+\cdot Cl^-\cdot 0.5H_2O$
$M_r = 171.60$
Orthorhombic, $Cmc2_1$
$a = 16.827$ (3) Å
$b = 12.300$ (2) Å
$c = 6.9898$ (14) Å
$V = 1446.6$ (5) Å$^3$
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.47$ mm$^{-1}$
$T = 210$ (2) K
0.20 × 0.18 × 0.15 mm

### *Data collection*

Stoe IPDS-II diffractometer
Absorption correction: none
8913 measured reflections
1317 independent reflections
1186 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$

### *Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.063$
$S = 1.03$
1317 reflections
105 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.20$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.21$ e Å$^{-3}$
Absolute structure: Flack (1983), with 595 Friedel pairs
Flack parameter: 0.11 (8)

**Table 1**
Selected bond angles (°).

| | | | |
|---|---|---|---|
| N2—C1—N6 | 125.59 (19) | C2—N2—C1 | 116.1 (2) |
| N2—C2—N4 | 121.0 (2) | C2—N4—C3 | 119.7 (2) |
| N6—C3—N4 | 121.4 (2) | C3—N6—C1 | 116.0 (2) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H$\cdots$*A* | *D*—H | H$\cdots$*A* | *D*$\cdots$*A* | *D*—H$\cdots$*A* |
|---|---|---|---|---|
| N1—H12$\cdots$Cl2$^{\rm i}$ | 0.86 | 2.44 | 3.281 (2) | 167 |
| N1—H11$\cdots$O1$^{\rm ii}$ | 0.86 | 2.23 | 3.044 (3) | 157 |
| N3—H32$\cdots$Cl1$^{\rm iii}$ | 0.86 | 2.48 | 3.256 (2) | 150 |
| N3—H31$\cdots$N6$^{\rm iv}$ | 0.86 | 2.18 | 3.038 (3) | 178 |
| N4—H4$\cdots$Cl1$^{\rm iii}$ | 0.86 | 2.47 | 3.246 (2) | 151 |
| N4—H4$\cdots$Cl1 | 0.86 | 3.02 | 3.350 (2) | 105 |
| N5—H52$\cdots$Cl2 | 0.86 | 2.48 | 3.259 (2) | 152 |
| N5—H51$\cdots$N2$^{\rm v}$ | 0.86 | 2.12 | 2.974 (3) | 175 |
| O1—H1$\cdots$Cl2$^{\rm vi}$ | 0.89 (5) | 2.41 (5) | 3.300 (4) | 176 (4) |
| O1—H2$\cdots$Cl1 | 0.81 (6) | 2.61 (5) | 3.321 (3) | 147 (5) |

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

All H atoms were located in a difference Fourier map. Those bonded to N were refined using a riding model with with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$ and N—H = 0.86 Å. The coordinates of the water H atoms were refined, but their $U_{\rm iso}({\rm H})$ values were set to $1.2U_{\rm eq}({\rm O})$.

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Data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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