

Melaminium chloride hemihydrate

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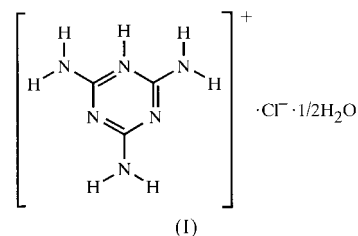
The crystals of a new melaminium salt, 2,4,6-triamino-1,3,5-triazin-1-ium chloride hemihydrate, $C_3H_7N_6^+ \cdot Cl^- \cdot 0.5H_2O$, are built up from single-protonated melaminium residues, chloride anions and water molecules. The protonated melaminium cations lie on a twofold axis, while the chloride anions and water molecule lie on the *m* plane. The melaminium residues are interconnected by N—H...N hydrogen bonds, forming chains parallel to the (001) plane. The chains of melaminium residues form a three-dimensional network through hydrogen-bond interactions with chloride anions and water molecules.

Comment

The present study is a continuation of our investigation of the characterization of hydrogen bonds formed by the melamine molecule in the solid state (Janczak & Perpétuo, 2001*a,b*). The melamine molecule and its organic and inorganic complexes or salts can develop supramolecular structures *via* multiple hydrogen-bonding systems by self-assembly of components which contain complementary arrays of hydrogen-bonding sites (MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). Solid-state properties, such as electrical conductivity, solid-state reactivity or non-linear optical properties, are influenced by the solid-state structure, *i.e.* the molecular structure and the orientation of the molecules with respect to each other in the crystal. Knowledge of the molecular architecture can provide a better understanding of the observed macroscopic properties of the crystals.

To expand the understanding of the solid-state physical-organic chemistry of compounds containing multiple and different hydrogen-bonding systems, we studied the solid-state structure of protonated melaminium chloride hemihydrate, (I). To our knowledge, this is the third structurally characterized melaminium salt which is protonated at only one ring N atom. The two previous structurally characterized compounds were the cocrystal of barbituric acid with mel-

amine (Zerkowski *et al.*, 1994) and melaminium phthalate (Janczak & Perpétuo, 2001*a*). In addition to these single-protonated melaminium salts, double-protonated melaminium salts have also been structurally characterized (Wang *et al.*, 1990; Martin & Pinkerton, 1995; Janczak & Perpétuo, 2001*b*).



The asymmetric unit of the title compound consists of two halves of melaminium residues, two halves of chloride anions and half a water molecule. The protonated melaminium cations lie on the twofold axis, while the chloride anions and water molecule lie on the *m* plane. The two melaminium residues (Fig. 1) do not differ significantly from one another.

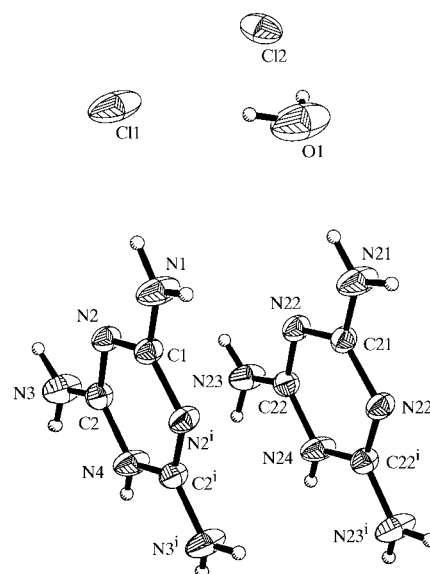


Figure 1

The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $-x, y, 1 - z$.]

The six-membered aromatic ring of both melaminium residues are similar and exhibit 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 of the ring. These differences are due to the steric effect of a lone pair of electrons and are fully consistent with the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992). A similar correlation between the internal C—N—C angles of the melaminium ring is observed in the crystal structure of the cocrystal of barbituric acid with melamine (Zerkowski *et al.*, 1994) and melaminium phthalate (Janczak & Perpétuo, 2001*a*). As a result of the protonation of the melamine ring at the N atom, the internal N—C—N angles involving the non-protonated ring N atoms are significantly greater than those containing protonated and non-protonated N atoms.

The melaminium residues are interconnected by four N—H···N hydrogen bonds, forming chains parallel to the (001) plane (Fig. 2). The chains are ~ 3.2 Å apart; this distance is shorter than the distance (~ 3.4 Å) between π -aromatic rings (Pauling, 1960) and indicates interaction between the melaminium rings of neighbouring chains. The chains of melaminium residues are interconnected by N—H···Cl and N—H···O hydrogen bonds, developing a three-dimensional supramolecular structure (Fig. 2). Each melaminium residue in the crystal is involved in 12 hydrogen bonds, *i.e.* four N—H···N bonds with two neighbouring melaminium residues, two N—H···O bonds with two distinct water molecules and six N—H···Cl bonds. Each H atom of the amine group *para* with respect to the protonated ring N atom is involved in one hydrogen bond with water. The H atom of the protonated ring N atom is involved in two hydrogen bonds with two chloride ions (Cl2 and its symmetry equivalent). One of the amine H atoms of the group *ortho* with respect to the protonated ring N atom is involved in two N—H···Cl hydrogen bonds, while the other forms one N—H···N bond with a neighbouring melamine residue (Fig. 2).

The Cl1 ion acts as an acceptor in four hydrogen bonds with four neighbouring melaminium residues, forming N—H···Cl bonds. Additionally, it interacts with one water H atom. The second chloride ion (Cl2) interacts with two neighbouring melaminium residues through the H atom of the protonated ring N atom and with two other melaminium residues through the H atom of the protonated ring N atom, as well as through one of the H atoms of the melaminium group.

The water molecule is involved as an acceptor in two hydrogen bonds with amine groups (*para* with respect to the protonated ring N atom) of two different melaminium resi-

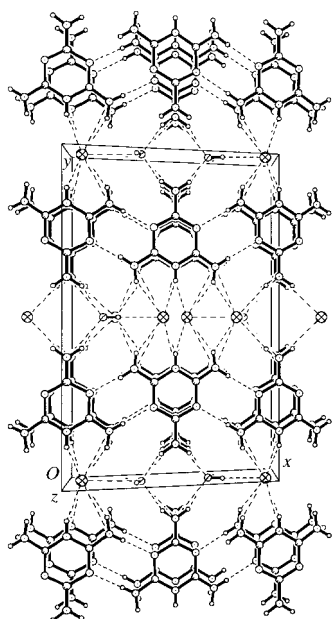


Figure 2

The molecular arrangement in the unit cell showing the hydrogen-bonding interactions (dashed lines).

dues and as a donor in hydrogen bonds with both chloride ions (Cl1 and Cl2). Details of the hydrogen-bonding geometry are given in Table 2.

Experimental

A 10% solution of HCl was added slowly to a solution of melamine in hot water. After several days, colourless crystals of the title salt appeared.

Crystal data

$C_3H_7N_6^+ \cdot Cl^- \cdot 0.5H_2O$
 $M_r = 343.21$
 Monoclinic, $C2/m$
 $a = 12.441$ (2) Å
 $b = 17.667$ (4) Å
 $c = 7.1370$ (10) Å
 $\beta = 114.99$ (3)°
 $V = 1421.8$ (4) Å³
 $Z = 4$
 $D_x = 1.603$ Mg m⁻³
 $D_m = 1.60$ Mg m⁻³

D_m , measured by flotation in a mixture of chloroform and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 1143 reflections
 $\theta = 3$ – 29°
 $\mu = 0.48$ mm⁻¹
 $T = 293$ (2) K
 Parallelepiped, colourless
 $0.33 \times 0.22 \times 0.16$ mm

Data collection

Kuma KM-4 diffractometer with two-dimensional CCD area-detector
 ω scans
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990)
 $T_{min} = 0.858$, $T_{max} = 0.927$

6439 measured reflections
 1870 independent reflections
 1143 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.012$
 $\theta_{max} = 29.1^\circ$
 $h = -16 \rightarrow 16$
 $k = -23 \rightarrow 23$
 $l = -8 \rightarrow 9$

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.314 (2)	N21—C21	1.309 (2)
Cl1—N2	1.360 (1)	C21—N22	1.362 (1)
N2—C2	1.324 (1)	N22—C22	1.320 (1)
C2—N3	1.318 (2)	C22—N23	1.318 (2)
C2—N4	1.365 (1)	C22—N24	1.365 (1)
N1—C1—N2	117.1 (1)	N21—C21—N22	117.3 (1)
N2 ⁱ —C1—N2	125.9 (1)	N22—C21—N22 ⁱⁱ	125.5 (1)
C2—N2—C1	115.8 (1)	C22—N22—C21	116.0 (1)
N3—C2—N2	120.5 (1)	N23—C22—N22	121.0 (1)
N3—C2—N4	118.2 (1)	N23—C22—N24	117.7 (1)
N2—C2—N4	121.3 (1)	N22—C22—N24	121.3 (1)
C2 ⁱ —N4—C2	120.0 (1)	C22—N24—C22 ⁱⁱ	119.9 (1)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1···Cl1	0.91 (1)	2.36 (1)	3.249 (1)	164 (1)
N3—H31···Cl1 ⁱ	0.83 (2)	2.52 (1)	3.166 (1)	135 (1)
N3—H32···N2 ⁱ	0.89 (2)	2.18 (1)	3.074 (1)	179 (1)
N4—H4···Cl2 ⁱⁱ	0.77 (2)	2.67 (1)	3.271 (1)	136 (1)
N21—H211···O1	0.89 (1)	2.09 (1)	2.940 (1)	159 (1)
N23—H231···Cl2 ⁱⁱⁱ	0.90 (2)	2.48 (1)	3.279 (1)	149 (1)
N23—H232···N22 ⁱⁱⁱ	0.86 (2)	2.16 (1)	3.023 (1)	176 (1)
N24—H24···Cl2 ⁱⁱⁱ	0.81 (2)	2.75 (1)	3.379 (1)	135 (1)
O1—H1O···Cl2	0.85	2.39	3.191 (2)	157
O1—H2O···Cl1	0.90	2.35	3.233 (2)	170

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.054$
 $S = 1.00$
1870 reflections
123 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0227P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

The positions of the H atoms of the melamine residues were refined ($U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent N atom), but the water H atoms were located from a difference Fourier map and were not refined ($U_{\text{iso}} = 1.5U_{\text{eq}}$ of the parent O atom).

Data collection: *KM-4 CCD Software* (Kuma, 1999); 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1530). Services for accessing these data are described at the back of the journal.

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