

## Bis(melaminium) sulfate dihydrate

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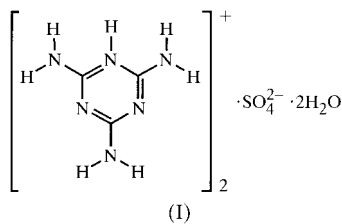
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The crystals of a new melaminium salt, bis(2,4,6-triamino-1,3,5-triazin-1-ium) sulfate dihydrate,  $2C_3H_7N_6^+ \cdot SO_4^{2-} \cdot 2H_2O$ , are built up from monoprotonated melaminium(1+) residues, sulfate(2-) anions and water molecules. The  $SO_4^{2-}$  ion has a slightly distorted tetrahedral geometry. The melaminium residues are interconnected by  $N-H \cdots N$  hydrogen bonds, forming chains. The chains of melaminium residues develop a three-dimensional network through multiple donor-acceptor hydrogen-bond interactions with sulfate anions and water molecules.

## Comment

The present study is a continuation of our characterization of the hydrogen bonds formed by the melamine molecule in the solid state (Janczak & Perpétuo, 2001*a,b,c*). The melamine molecule and its derivatives, as well as its organic and inorganic complexes or salts, can develop supramolecular structures *via* a multiple hydrogen-bonding system 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 present here the solid-state structure of bis(melaminium) sulfate dihydrate, (I).



The asymmetric unit of the title compound consists of two melaminium residues protonated at one ring N atom, a sulfate anion and two water molecules (Fig. 1). The protonated

melaminium residues do not differ significantly. The six-membered aromatic rings of the 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 significantly greater than the other two C–N–C angles within the rings. This is a result of the steric effect of a lone pair of electrons and is fully consistent with the valence-shell electron pair repulsion (VSEPR) theory (Gillespie, 1963). The correlation between the internal C–N–C angles within the melaminium ring is quite similar to that reported for barbituric acid with melamine (Zerkowski *et al.*, 1994), melaminium phthalate (Janczak & Perpétuo, 2001*a*) and melaminium chloride hemihydrate (Janczak & Perpétuo, 2001*c*), the three monoprotonated melaminium salts that have been structurally characterized previously. As a result of the protonation of one of the melamine ring N atoms, the internal N–C–N angle containing only non-protonated N atoms is significantly greater than both N–C–N angles containing protonated and non-protonated N atoms.

The melaminium *M1* residue (C1–C3/N1–N6) in the crystal is involved in nine hydrogen bonds, *i.e.* four  $N-H \cdots N$  bonds with two neighbouring melaminium residues (*M1* and *M2*) and five  $N-H \cdots O$  bonds with four neighbouring  $SO_4^{2-}$  anions. One of the  $SO_4^{2-}$  anions is an acceptor of two hydrogen bonds, while the other three are acceptors of one hydrogen bond each. The second melaminium residue, *M2* (C21–C23/N21–N26), similar to *M1*, forms four  $N-H \cdots N$  hydrogen bonds with two neighbouring melaminium residues and five  $N-H \cdots O$  hydrogen bonds with two different  $SO_4^{2-}$  anions and three distinct water molecules. The H atom at the protonated N atom of the melaminium *M1* residue is involved in a slightly bent [ $168(2)^\circ$ ]  $N-H \cdots O$  hydrogen bond with the O1 atom of the  $SO_4^{2-}$  ion, while the H atom at the protonated N atom of the melaminium *M2* residue is involved in an almost linear [ $177(2)^\circ$ ]  $N-H \cdots O$  hydrogen bond with the water O5 atom.

The sulfate anion has an expected but slightly distorted tetrahedral geometry, with the S–O bond lengths ranging from 1.450 (1) to 1.483 (1) Å and the O–S–O bond angles ranging from 108.43 (7) to 110.80 (8)°. The differences between the S–O bonds of the  $SO_4^{2-}$  ion correlate well with the number and strength of the hydrogen bonds formed by the O atoms. The O2 atom, which has the longest S–O bond, is

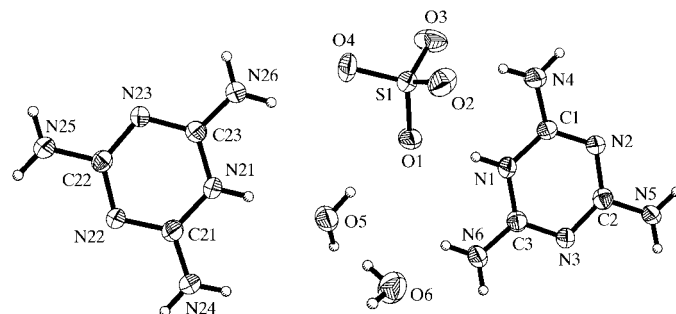
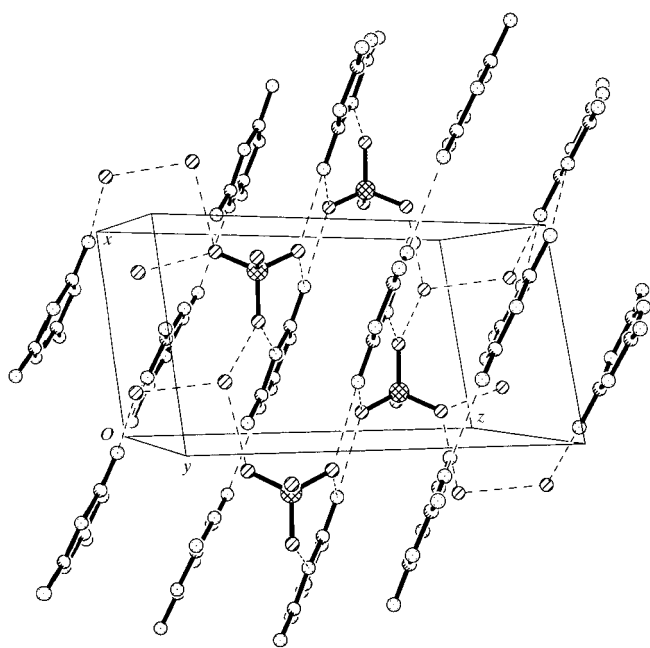


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

involved in the shortest hydrogen bond. The  $\text{SO}_4^{2-}$  ion is involved as acceptor in nine hydrogen bonds. These bonds involve five melaminium residues (three  $M1$  and two  $M2$ ) and three water molecules. The O2 atom is the most interesting as it accepts three hydrogen bonds, two from water molecules and one from the amine group of the melaminium  $M2$  residue. The other three O atoms of the  $\text{SO}_4^{2-}$  ion are involved in two hydrogen bonds. The O3 atom is involved as acceptor in two hydrogen bonds with two melaminium  $M1$  residues, while O4 forms two hydrogen bonds with two different melaminium residues ( $M1$  and  $M2$ ) via the H atoms of the melamine groups. The O1 atom forms hydrogen bonds with the H1 atom at the protonated N atom of the melaminium  $M1$  residue and with the water H1O5 atom.



**Figure 2**  
The molecular arrangement in the unit cell showing the hydrogen-bonding interactions (dashed lines).

The water molecules form a hydrogen-bonded dimeric structure ( $\text{O6}-\text{H}_2\text{O}6\cdots\text{O5}$ ) which joins three  $\text{SO}_4^{2-}$  ions and three melaminium  $M2$  residues and do not form any hydrogen bonds with melaminium  $M1$  residues. The O5 water molecule as donor forms two  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds with two  $\text{SO}_4^{2-}$  ions and as acceptor forms one hydrogen bond with the melaminium  $M2$  residue via the H atom at the protonated ring-N atom, while the O6 water molecule is involved as acceptor in hydrogen bonds with two melaminium  $M2$  residues via the H atoms of the amine groups and as donor forms a hydrogen bond with O2 of the  $\text{SO}_4^{2-}$  ion. Details of the hydrogen-bonding geometry are given in Table 2. The most noticeable feature of the structure is that the interaction between the water molecules and sulfate ions in the crystal leads to the formation of  $\{\text{SO}_4^{2-}(\text{H}_2\text{O})_2\}_n$  chains that are almost parallel to the  $x$  axis ( $\sim 13.5^\circ$ ).

In the crystal, the melaminium residues are interconnected by four almost linear  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds [ $\text{N}-\text{H}\cdots\text{N}$  angles range from  $171(2)$  to  $178(2)^\circ$ ] that form  $(M1M1M2M2)_n$  chains which are inclined by  $\sim 23$ ,  $\sim 27$  and  $\sim 53^\circ$  to the  $x$ ,  $y$  and  $z$  axes, respectively. These chains are separated by  $\sim 3.5 \text{ \AA}$ , slightly longer than the distance ( $\sim 3.4 \text{ \AA}$ ) between  $\pi$ -aromatic rings (Pauling, 1960), indicating a weaker interaction between the melaminium rings of neighbouring chains. The chains of melaminium cations are extensively interconnected by multiple hydrogen bonds with water molecules and sulfate anions, developing a three-dimensional supramolecular structure (Fig. 2).

### Experimental

Melamine was dissolved in a 20% solution of  $\text{H}_2\text{SO}_4$  and the resulting solution was evaporated slowly. After several days, colourless crystals of the title salt appeared.

#### Crystal data

$2\text{C}_3\text{H}_7\text{N}_6^+\cdot\text{SO}_4^{2-}\cdot 2\text{H}_2\text{O}$   
 $M_r = 386.38$   
 Triclinic,  $P\bar{1}$   
 $a = 6.4460(10) \text{ \AA}$   
 $b = 10.457(2) \text{ \AA}$   
 $c = 12.363(2) \text{ \AA}$   
 $\alpha = 104.28(3)^\circ$   
 $\beta = 92.16(3)^\circ$   
 $\gamma = 103.81(3)^\circ$   
 $V = 780.1(2) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.645 \text{ Mg m}^{-3}$

$D_m = 1.64 \text{ Mg m}^{-3}$   
 $D_m$  measured by flotation in a chloroform/bromoform mixture  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1890 reflections  
 $\theta = 3-28^\circ$   
 $\mu = 0.27 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Parallelepiped, colourless  
 $0.32 \times 0.27 \times 0.23 \text{ mm}$

#### Data collection

Kuma KM-4 with CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: face-indexed analytical (SHELXTL; Sheldrick, 1990)  
 $T_{\min} = 0.919$ ,  $T_{\max} = 0.941$   
 7091 measured reflections

3659 independent reflections  
 1890 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 28.2^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -13 \rightarrow 13$   
 $l = -16 \rightarrow 14$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S1—O4	1.450 (1)	N5—C2	1.320 (2)
S1—O3	1.456 (1)	N6—C3	1.318 (2)
S1—O1	1.478 (1)	N21—C21	1.356 (2)
S1—O2	1.483 (1)	N21—C23	1.359 (2)
N1—C3	1.354 (2)	N22—C21	1.332 (2)
N1—C1	1.365 (2)	N22—C22	1.348 (2)
N2—C1	1.323 (2)	N23—C23	1.336 (2)
N2—C2	1.344 (2)	N23—C22	1.342 (2)
N3—C3	1.328 (2)	N24—C21	1.310 (2)
N3—C2	1.359 (2)	N25—C22	1.328 (2)
N4—C1	1.313 (2)	N26—C23	1.305 (2)
O4—S1—O3	110.80 (8)	N2—C1—N1	121.4 (2)
O4—S1—O1	110.30 (7)	N2—C2—N3	125.9 (2)
O3—S1—O1	108.43 (7)	N3—C3—N1	121.3 (2)
O4—S1—O2	109.19 (7)	C21—N21—C23	119.8 (2)
O3—S1—O2	109.15 (8)	C21—N22—C22	115.9 (2)
O1—S1—O2	108.93 (7)	C23—N23—C22	115.5 (2)
C3—N1—C1	119.7 (2)	N22—C21—N21	121.1 (2)
C1—N2—C2	115.9 (2)	N23—C22—N22	126.3 (2)
C3—N3—C2	115.7 (2)	N23—C23—N21	121.4 (2)

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.038$   
 $S = 0.99$   
 3659 reflections  
 281 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.006P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0149 (5)

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O1$	0.87 (2)	1.91 (2)	2.767 (2)	169 (2)
$N4-H4A \cdots O3^i$	0.86 (2)	2.03 (2)	2.769 (2)	145 (2)
$N4-H4B \cdots O3$	0.85 (2)	2.04 (2)	2.884 (2)	172 (2)
$N5-H5A \cdots N2^{ii}$	0.86 (2)	2.27 (2)	3.122 (2)	174 (2)
$N5-H5B \cdots O4^{iii}$	0.87 (2)	2.18 (2)	3.030 (2)	164 (2)
$N6-H6A \cdots N23^{iii}$	0.85 (2)	2.22 (2)	3.065 (2)	178 (2)
$N6-H6B \cdots O2^{iv}$	0.84 (2)	2.51 (2)	3.074 (2)	126 (2)
$N21-H21 \cdots O5$	0.89 (2)	1.89 (2)	2.776 (2)	177 (2)
$N24-H24A \cdots N22^v$	0.88 (2)	2.09 (2)	2.954 (2)	171 (2)
$N24-H24B \cdots O6^{vi}$	0.85 (2)	2.16 (2)	2.859 (2)	139 (2)
$N25-H25A \cdots O2^{vii}$	0.88 (2)	2.11 (2)	2.972 (2)	168 (2)
$N25-H25B \cdots O6^{vii}$	0.85 (2)	2.21 (2)	3.039 (2)	165 (2)
$N26-H26A \cdots N3^{viii}$	0.89 (2)	2.04 (2)	2.917 (2)	172 (2)
$N26-H26B \cdots O4$	0.88 (2)	1.99 (2)	2.707 (2)	138 (2)
$O5-H1O5 \cdots O1$	0.84 (2)	1.90 (2)	2.737 (2)	175 (2)
$O5-H2O5 \cdots O2^{iv}$	1.01 (2)	1.81 (2)	2.798 (2)	166 (2)
$O6-H1O6 \cdots O2^{ix}$	0.83 (2)	2.24 (2)	3.028 (2)	160 (2)
$O6-H2O6 \cdots O5$	0.88 (2)	2.02 (2)	2.887 (2)	169 (2)

Symmetry codes: (i)  $-x, 1-y, 1-z$ ; (ii)  $1-x, 2-y, 1-z$ ; (iii)  $1+x, 1+y, z$ ; (iv)  $1+x, y, z$ ; (v)  $2-x, -y, 2-z$ ; (vi)  $2-x, 1-y, 2-z$ ; (vii)  $x, y-1, z$ ; (viii)  $x-1, y-1, z$ ; (ix)  $1-x, 1-y, 2-z$ .

The positions of the H atoms of the melamine residues were refined [ $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$ ; see Table 2 for distances], but the water H atoms were located from a difference Fourier map and were constrained [ $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$ ].

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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1499). Services for accessing these data are described at the back of the journal.

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