Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Three-dimensional hydrogen-bonded framework in bis(melamin-1-ium) naphthalene-1,5-disulfonate melamine pentahydrate

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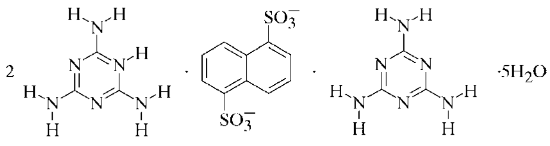
Received 12 December 2007
Accepted 7 January 2008
Online 22 January 2008

Crystals of the title compound, $2C_3H_7N_6^+\cdot C_{10}H_6O_6S_2^{2-}\cdot C_3H_6N_6\cdot 5H_2O$, are built up of neutral 2,4,6-triamino-1,3,5-triazine (melamine), singly protonated melaminium cations, naphthalene-1,5-disulfonate dianions and water molecules. Two independent anions lie across centres of inversion in the space group $P\overline{1}$. The melamine molecules are connected by N—H···N hydrogen bonds into two different one-dimensional polymers almost parallel to the (010) plane, forming a stacking structure along the *b* axis. The centrosymmetric naphthalene-1,5-disulfonate anions interact with water molecules *via* O—H···O hydrogen bonds, forming layers parallel to the (001) plane. The cations and anions are connected by N—H···O and O—H···N hydrogen bonds to form a three-dimensional supramolecular framework.

Comment

The present study is a continuation of our investigations of the hydrogen-bonding systems formed by triazine derivatives in the solid state (Perpétuo & Janczak, 2007; Janczak & Kubiak, 2005*a*,*b*). Triazine and its derivatives, especially 2,4,6-triamino-1,3,5-triazine (melamine) and its organic and inorganic complexes or salts, are widely used in crystal engineering to build up extended frameworks, since they contain components of complementary arrays of hydrogen-bonding sites (Janczak & Perpétuo, 2003, 2004; Desiraju, 2002; Sherrington & Taskinen, 2001; Krische & Lehn, 2000; Row, 1999; MacDonald & Whitesides, 1994). Hydrogen bonds are widely used as the principal interactions in crystal engineering since they are directional and relatively strong (Steiner, 2002; Moulton & Zaworotko, 2001; Desiraju, 1990). Our interest in these types of compounds arises from the possibility of obtaining materials suitable for nonlinear optics (Janczak & Perpétuo, 2002; Marchewka *et al.*, 2003; Perpétuo & Janczak, 2006). In order to expand the understanding of the solid-state physical–organic chemistry of compounds that form multiple N—H···N and N—H···O hydrogen-bonding systems, we present here the solid-state structure of bis(melamin-1-ium) naphthalene-1,5-disulfonate (1,5-NDS) melamine pentahydrate, (I).



(I)

The asymmetric unit of (I) consists of a neutral melamine molecule, two melaminium cations, each singly protonated at one of three ring N atoms, five water molecules, all in general positions, and two independent anions, each lying across a centre of inversion (Fig. 1). Thus, (I) is an example of a compound containing both a neutral melamine molecule and protonated melaminium cations, and to the best of our knowledge it is only the second example of this type (Cambridge Structural Database, Version 5.29 of November 2007; Allen, 2002).

The triazine rings of the neutral melamine molecule and the two protonated melaminium cations are essentially planar [the deviation of the N and C atoms from the mean plane is less than 0.033 (3) Å], but both exhibit significant distortion from the ideal hexagonal form (Table 1). In the neutral melamine molecule, the internal C—N—C angles are significantly greater than 120° and the internal N—C—N angles are significantly smaller than 120°. However, in the protonated melaminium units, only the C—N—C angles at the non-protonated N atoms are smaller than 120°, while the C—N—C angles at the protonated ring atoms are almost equal to 120°. This distortion results from the steric effect of the lone-pair electrons, predicted by the valence-shell electron-pair repulsion model (Gillespie, 1963, 1992), according to which the lone pair of electrons on the ring N atoms occupies a wider region than the N—H bonding pair, causing the internal angle of the latter to be greater than on the nonprotonated ring N atoms. As a result of the protonation of the triazine ring at one of three ring N atoms, the internal N—C—N angle involving only nonprotonated N atoms is significantly greater than the remaining two N—C—N angles involving both protonated and nonprotonated N atoms (Table 1).

The gas-phase geometry calculated *ab initio* for an isolated neutral melamine molecule and for a singly protonated melaminium cation shows similar trends in the internal C—N—C and N—C—N angles within the ring (Drozd & Marchewka, 2005). Thus, the ring distortions result mainly from the steric effect of a lone pair of electrons and additionally in melaminium cations from the protonation and, to a lesser degree, from the hydrogen-bonding system, interionic interactions and crystal packing forces. Protonation of the triazine ring also disturbs the C—N bonds within the ring when compared with the neutral 2,4,6-triamino-1,3,5-triazine molecule (Aoki *et al.*, 1994).

The two 1,5-NDS anions are quite similar with regard to bond lengths and angles. However, a small difference caused by the hydrogen-bonding interaction can be found in the orientation of the SO_3 group in relation to the naphthalene ring system. The O3—S1—C2—C1 torsion angle is 0.6 (1)°, while in the second dianion the respective O5—S2—C7—C6 torsion angle is −10.2 (1)°. The S—O distances in both 1,5-NDS anions, with an average value of 1.456 Å, are intermediate between double S═O and single S—O bonds (Allen *et al.*, 1987), indicating charge delocalization on all O atoms in the SO_3 groups. The average C—S bond length of 1.775 (3) Å in (I) is comparable with those found in naphthalene-1,5-disulfonic acid tetrahydrate, in which the H atoms are transferred to the water molecules forming H_5O^+ cations (Perpétuo & Janczak, 2008). The C—S bond length in the crystal structure of (I) is shorter than those for the gas-phase structure obtained by molecular orbital calculations (1.841 Å), due to the interaction of the negatively charged SO_3 groups with the π-aromatic ring system (Perpétuo & Janczak, 2008). In the crystal structure, this interaction is diminished due to the hydrogen-bonding system, which reduces the charge on the SO_3 groups.

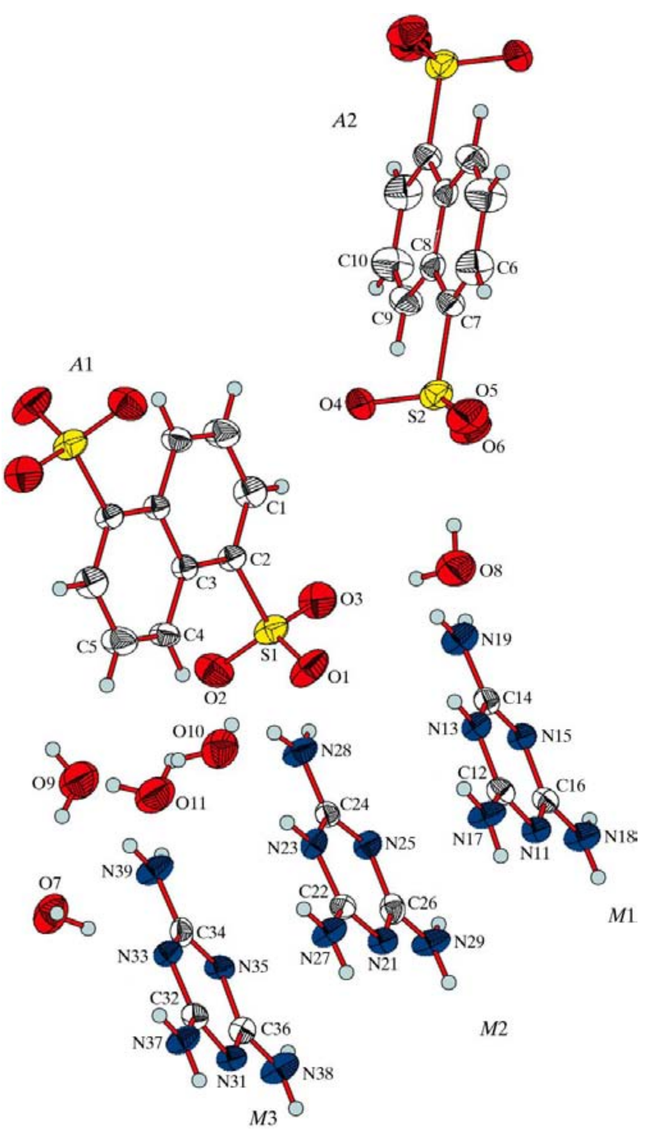


Figure 1

A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The melamine molecules of (I) are interconnected by two pairs of almost linear N—H···N hydrogen bonds forming two different one-dimensional polymers, each characterized by an $R_2^2(8)$ motif, which is one of the 24 most frequently observed bimolecular cyclic hydrogen-bonded units in organic crystal structures (Steiner, 2002). One of the chains contains only protonated melaminium cations ($M1^+$), while the other contains both neutral melamine ($M3$) and melaminium ($M2^+$) residues which alternate along the chain. Both chains run parallel to the [100] direction and they are stacked along [010] (Fig. 2). Within the stacks, the two types of melamine chain alternate, and the average distance between the planes of the $(M3M2^+)_n$ and $(M1^+M1^+)_n$ chains is shorter (~3.25 Å) than that between the $(M3M2^+)_n$ and $(M3M2^+)_n$ chains (~3.40 Å), indicating π–π interactions between the aromatic triazine rings. This distance is comparable with the sum of the van der Waals radii of C and N atoms of the π-aromatic ring system (Pauling, 1967) and longer than the distance at which the steric interaction between the π-aromatic ring system becomes predominantly repulsive (~3.08 Å; Scheidt & Lee, 1987).

The centrosymmetric 1,5-NDS anions are joined by the water molecules into a sheet parallel to the (001) plane (Fig. 2). The water molecules containing atoms O7, O9 and O10 are joined together by O—H···O hydrogen bonds into a trimeric structure (O7···O9···O10). The water molecules containing atoms O8 and O11 do not interact with other water molecules, but act as donors to the anions only and as acceptors from melamine molecules only. The trimeric structure of water molecules acts as a donor in hydrogen bonds with three 1,5-NDS anions, namely two 1,5-NDS anions *A*2 and one *A*1 (where *A*1 contains atom S1 and *A*2 contains atom S2). In

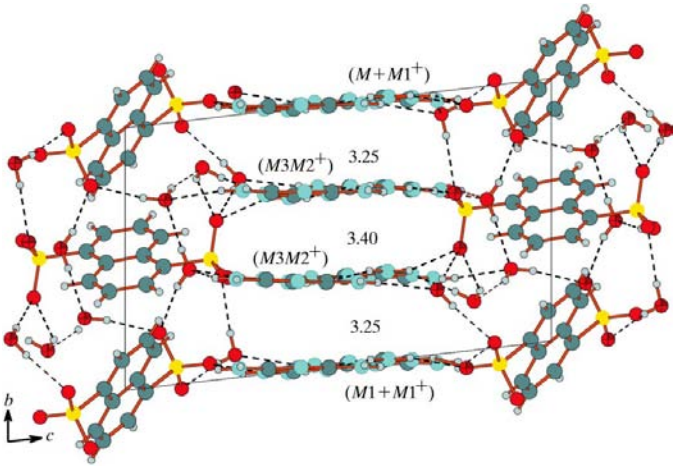


Figure 2

A view of the crystal packing in (I), showing the stack of melaminium molecules and the hydrogen-bonded sheets of anions and water molecules. Distances are given in Å.

addition, water atom O9 is the acceptor in a hydrogen bond with a neutral melamine molecule, while water atoms O7 and O10 act as acceptors in hydrogen bonds with different melaminium cations, *viz*. O7 with N19 and O10 with N28. Thus, the O atoms in the trimeric structure of water molecules possess distorted tetrahedral environments. Water atoms O8 and O11 also exhibit tetrahedral environments, since they each act as donor and acceptor in two hydrogen bonds, O8 as donor to two different 1,5-NDS anions (*A*1 and *A*2) and as acceptor from two symmetry-equivalent melaminium cations (with NH_2 groups N18 and N19), and O11 as donor to two different 1,5-NDS anions (*A*1 and *A*2) and as acceptor from both a neutral melamine molecule and a melaminium cation (in both it forms a hydrogen bond with an amine group). The positively charged melamine stacks and the negatively charged sheets of anions and water molecules are linked by N—H···O and O—H···O hydrogen bonds to form a three-dimensional supramolecular framework structure (Fig. 2 and Table 2).

Experimental

2,4,6-Triamino-1,3,5-triazine (98%) was dissolved in a 10% aqueous solution of naphthalene-1,5-disulfonic acid. After several days, colourless crystals of (I) had formed, which proved to be suitable for single-crystal X-ray diffraction analysis.

Crystal data

$2C_3H_7N_6^+\cdot C_{10}H_6O_6S_2^{2-}\cdot C_3H_6N_6\cdot 5H_2O$
$M_r = 756.78$
Triclinic, $P\overline{1}$
$a = 10.8320\ (18)$ Å
$b = 10.9131\ (19)$ Å
$c = 16.470\ (3)$ Å
$\alpha = 77.302\ (11)^\circ$
$\beta = 74.481\ (12)^\circ$
$\gamma = 63.112\ (11)^\circ$
$V = 1662.0\ (5)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 295\ (2)$ K
$0.40 \times 0.38 \times 0.14$ mm

Data collection

Kuma KM-4 diffractometer with CCD area-detector
Absorption correction: analytical [face-indexed; *SHELXTL* (Sheldrick, 2008)]
$T_{min} = 0.911$, $T_{max} = 0.969$
22496 measured reflections
8240 independent reflections
4664 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.088$
$S = 1.00$
8240 reflections
481 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.450 (2)	S2—O6	1.450 (2)
S1—O1	1.454 (2)	S2—O4	1.453 (2)
S1—O2	1.460 (2)	S2—O5	1.469 (2)
S1—C2	1.771 (3)	S2—C7	1.779 (3)
C12—N11—C16	115.2 (2)	N25—C24—N23	122.0 (3)
N11—C12—N13	121.6 (3)	C24—N25—C26	114.9 (2)
C12—N13—C14	119.5 (2)	N21—C26—N25	126.6 (3)
N15—C14—N13	121.3 (3)	C32—N31—C36	113.3 (2)
C14—N15—C16	115.7 (2)	N33—C32—N31	126.6 (3)
N15—C16—N11	126.6 (3)	C32—N33—C34	114.2 (2)
C22—N21—C26	115.5 (2)	N35—C34—N33	125.7 (2)
N21—C22—N23	121.2 (3)	C34—N35—C36	113.9 (2)
C24—N23—C22	119.7 (2)	N31—C36—N35	126.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N13—H13···O6^{i}	0.86	2.08	2.833 (3)	146
N17—H17*A*···N11^{ii}	0.86	2.17	3.024 (3)	172
N17—H17*B*···O6^{i}	0.86	2.15	2.899 (3)	145
N18—H18*A*···N15^{iii}	0.86	2.19	3.050 (3)	177
N18—H18*B*···O8^{iii}	0.86	2.31	2.970 (3)	134
N19—H19*A*···O8	0.86	2.18	3.030 (4)	168
N23—H23···O10	0.86	1.96	2.742 (3)	151
N27—H27*A*···N31^{iv}	0.86	2.09	2.936 (3)	168
N27—H27*B*···O3^{i}	0.86	2.03	2.874 (3)	168
N28—H28*A*···O1	0.86	2.02	2.864 (3)	167
N28—H28*B*···O10	0.86	2.14	2.887 (3)	144
N29—H29*A*···O11^{v}	0.86	2.21	2.945 (3)	143
N29—H29*B*···N35^{v}	0.86	2.13	2.983 (3)	173
N37—H37*A*···O2^{i}	0.86	2.25	3.073 (3)	160
N37—H37*B*···N21^{iv}	0.86	2.24	3.080 (3)	167
N38—H38*A*···O1^{v}	0.86	2.50	3.098 (3)	127
N38—H38*B*···N25^{v}	0.86	2.24	3.102 (3)	179
N39—H39*A*···O11	0.86	2.28	3.114 (3)	164
N39—H39*B*···O9	0.86	2.33	3.180 (4)	171
O7—H71···N33	0.82	1.98	2.783 (3)	165
O7—H72···O2^{i}	0.82	2.26	2.944 (3)	142
O8—H81···O3	0.82	2.21	3.011 (3)	168
O8—H82···O5	0.82	2.14	2.947 (3)	168
O9—H91···O7	0.82	1.96	2.741 (3)	160
O9—H92···O4^{vi}	0.82	2.05	2.850 (3)	164
O10—H101···O9	0.82	1.96	2.766 (4)	167
O10—H102···O4^{i}	0.82	1.97	2.774 (3)	166
O11—H111···O5^{vii}	0.82	2.07	2.891 (3)	174
O11—H112···O2	0.82	2.03	2.848 (3)	173

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

All H atoms were located in difference maps and then treated as riding atoms, with distances C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{iso}(H) = kU_{eq}$(carrier), where $k = 1.2$ for H atoms bonded to C and 1.5 for H atoms bonded to N or O atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

This work was supported financially by the Ministry of Science and Information Society Technologies (project No. 3T09A12128).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3182). Services for accessing these data are described at the back of the journal.

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