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Melaminium bis(4-hydroxybenzenesulfonate) dihydrate

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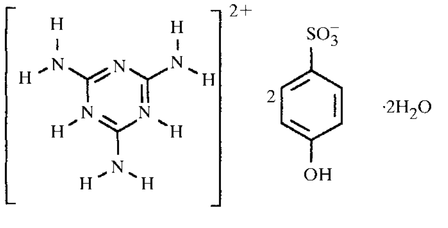
The crystals of a new melaminium salt, 2,4,6-triamino-1,3,5-triazine-1,3-diium bis(4-hydroxybenzenesulfonate) dihydrate, $C_3H_8N_6^{2+}\cdot 2C_6H_5O_4S^-\cdot 2H_2O$, are built up from doubly protonated melaminium(2+) residues, dissociated *p*-phenolsulfonate anions and water molecules. The doubly protonated melaminium dication lies on a twofold axis. The hydroxyl group of the *p*-hydroxybenzenesulfonate residue is roughly coplanar with the phenyl ring [dihedral angle 13 (2)°]. A combination of ionic and donor–acceptor hydrogen-bond interactions link the melaminium and *p*-hydroxybenzenesulfonate residues and the water molecules to form a three-dimensional network.

Comment

This study is a continuation of our investigation into the characterization of the hydrogen bonds formed by the melamine molecule in the solid state (Janczak & Perpétuo, 2001). To expand the understanding of the solid-state physical–organic chemistry of compounds containing N—H···O and O—H···O hydrogen bonds, we have studied the solid-state structure of the title diprotonated compound, melaminium *p*-hydroxybenzenesulfonate dihydrate, (I).



(I)

The crystal of (I) consists of water molecules and two well defined oppositely charged residues, namely, a moiety protonated at two of the three N atoms of the melaminium ring and dissociated *p*-hydroxybenzenesulfonate ions. However, the asymmetric unit consists of only half of a diprotonated melaminium residue, one *p*-hydroxybenzenesulfonate anion and one water molecule (Fig. 1). To our knowledge, this is the third structurally characterized melaminium salt which is protonated at two ring N atoms; the first was the hydrochloride of a melaminium–cyanuric acid complex (Wang *et al.*, 1990) and the second was a hydrated complex of perchlorate acid with melamine (Martin & Pinkerton, 1995). In addition to these doubly protonated melaminium salts, singly protonated melaminium salts have also been structurally characterized (Zerkowski *et al.*, 1994; Janczak & Perpétuo, 2001).

The six-membered aromatic ring of the melaminium residue, $C_3H_8N_6^{2+}$, is almost planar. Two of the three amino groups are approximately coplanar with the weighted least-squares plane through the melaminium ring, while the third group (at N4) is rotated along the C8—N4 bond by 13 (2)°. This is probably due to an H1N1···H1N4 interaction of 2.30 (2) Å, caused by the fact that C8 is bonded to both protonated N atoms of the melaminium ring and is involved in the intermolecular hydrogen-bonding system.

The ring of the melaminium residue is significantly distorted from the ideal hexagonal form. The internal C—N—C angle at the non-protonated N atom is significantly smaller than the C—N—C angles at the protonated N atoms. These differences between the internal C—N—C angles within the melaminium ring residue correlate with the steric effect of the lone-pair electrons and are fully consistent with the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1972). Protonation of the melamine ring at two N atoms distorts the bond lengths in the aromatic ring. The two shortest bonds in the melaminium ring (N2—C7 and its symmetrical equivalent) are those farthest from the protonated ring N atoms. The two longest N—C bonds of the melaminium ring (N1—C7 and its symmetrical equivalent) are those connected to the shortest bonds. This has the effect of opening up the ring bond angles at C7 and its symmetrical equivalent. A semi-empirical calculation performed with the *AM*1 parameter set (Dewar *et al.*, 1985) on the melaminium residue doubly protonated at two ring N atoms results in almost the same geometrical features. Thus, the ring distortion of the melaminium residue mainly results from the protonation and, to a lesser degree, from the hydrogen bonding and crystal packing. The distor-

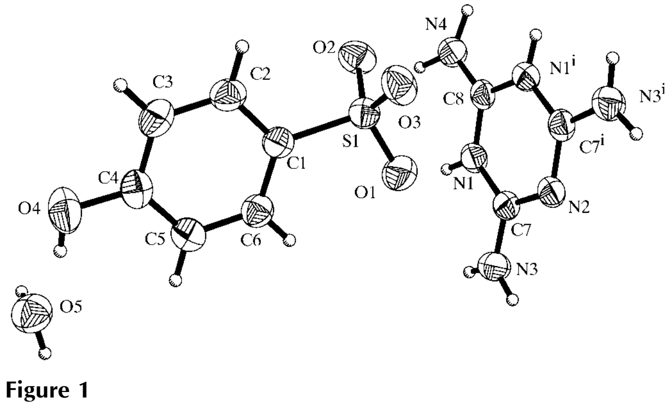


Figure 1
The molecular structure of the asymmetric unit of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

tion of the aromatic melaminium ring in (I) is quite similar to that reported for the hydrochloride of the melamine–cyanuric acid complex (Wang *et al.*, 1990), as well as for the melaminium diperchlorate monohydrate complex (Martin & Pinkerton, 1995), *i.e.* both of the simple salts of diprotonated melamine that have been reported previously.

The ring of the *p*-hydroxybenzenesulfonate anion shows a slight quinone character. This is probably due to the substitution effect of the hydroxyl and sulfonate groups in the 1,4-positions of the ring. The C—O (OH group) and C—S (SO_3^- group) bond lengths are comparable with the distances of 1.364 (15) and 1.750 (8) Å observed for $C_{aromatic}$—O and $C_{aromatic}$—S bonds, respectively (Allen *et al.*, 1987). The hydroxyl group is roughly coplanar with the ring [C5—C4—O4—H1O4 −13 (2)°]. The sulfonate group has a slightly distorted tetrahedral geometry and is oriented so that the S1—O1 bond is almost coplanar with the phenyl ring [C2—C1—S1—O1 175.6 (1)°]. The differences between the S—O bond lengths of the SO_3^- group are correlated with the number and strength of the hydrogen bonds formed by the O atoms. The O atom of the longest S—O bond is involved in three hydrogen bonds as acceptor, while the other two O atoms are involved as acceptors in only one hydrogen bond. Although atoms O1 and O2 are involved in only one hydrogen bond, the S1—O1 and S1—O2 bond lengths are different, S1—O1 being shorter than S1—O2, since O1 forms a weaker hydrogen bond than O2.

Both oppositely charged residues and the water molecules interact extensively by a combination of ionic and donor–acceptor hydrogen-bond interactions throughout the lattice to form a three-dimensional network (Fig. 2). All eight H atoms of the melaminium residue form hydrogen bonds with four different *p*-hydroxybenzenesulfonate anions and with two water molecules, which are acceptors of hydrogen bonds. Two of these four *p*-hydroxybenzenesulfonate residues are involved as acceptors in two hydrogen bonds with a melaminium residue (N1—H1N1···O2 and N4—H1N4···O3), while the other two *p*-hydroxybenzenesulfonate moieties are involved in only one hydrogen bond with the same melaminium residue. Thus, one melaminium residue forms eight hydrogen bonds. There are six N—H···O hydrogen bonds with four neighbouring *p*-hydroxybenzenesulfonate anions, and the other two H atoms of the melaminium residue form hydrogen bonds with the water molecules. The most noticeable feature is the fact that the non-protonated N atom of the melaminium residue is not involved as an acceptor in any hydrogen bond.

The SO_3^- group of the *p*-hydroxybenzenesulfonate residue is involved as an acceptor in three O···H—N hydrogen bonds from two different melaminium moieties and in two O···H—O hydrogen bonds with two water molecules, while the hydroxyl group of the *p*-hydroxybenzenesulfonate ion (as a donor) forms a hydrogen bond with a water molecule. Thus, one *p*-hydroxybenzenesulfonate residue is involved in six different hydrogen bonds.

The water molecule is involved as a donor in two hydrogen bonds with the SO_3^- groups of two different *p*-hydroxybenzenesulfonate anions, and as an acceptor in hydrogen bonds with the phenol hydroxyl group and with the N3 amino group from a melaminium dication.

In the crystal of (I), the melaminium residues form layers which are *a*/2 apart. In one layer, the melaminium residues are parallel to each other. The ring of the melaminium residue is perpendicular to the *ac* plane and forms angles of about 36 and 54° with the *bc* and *ab* planes, respectively. The ring of the *p*-hydroxybenzenesulfonate anion is almost perpendicular to the *bc* plane and makes a dihedral angle of 60.6° with the *ab* plane and 28.5° with the *ac* plane. The plane of the melaminium residue is inclined at an angle of 72.2 (1)° to the plane of the *p*-hydroxybenzenesulfonate ring. Details of the hydrogen-bonding geometry are given in Table 2.

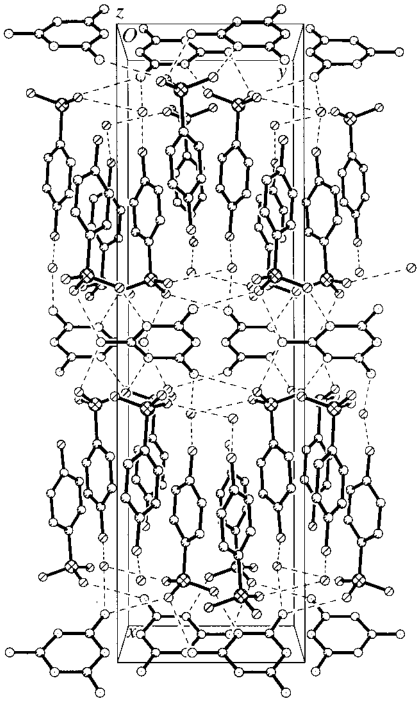


Figure 2
The molecular arrangement in the unit cell of (I) showing the hydrogen-bonding interactions (dashed lines). H atoms have been omitted for clarity.

Experimental

Melamine was dissolved in hot water and to this solution was slowly added a 10% solution of *p*-hydroxybenzenesulfonic acid. After several days, colourless crystals of (I) appeared.

Crystal data

$C_3H_8N_6^{2+}\cdot 2C_6H_5O_4S^-\cdot 2H_2O$
M_r = 510.51
Orthorhombic, *Pbcn*
a = 26.625 (5) Å
b = 7.863 (2) Å
c = 10.230 (2) Å
V = 2141.7 (8) Å^3
Z = 4
D_x = 1.583 Mg m^{-3}
D_m = 1.58 Mg m^{-3}
D_m measured by flotation
Mo *Kα* radiation
Cell parameters from 2155 reflections
θ = 5–26°
μ = 0.32 mm^{-1}
T = 293 (2) K
Parallelepiped, colourless
0.28 × 0.24 × 0.16 mm

Data collection

Kuma KM-4 diffractometer with a two-dimensional CCD area-detector
ω scans
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min} = 0.917$, $T_{\max} = 0.951$

17 563 measured reflections
2806 independent reflections
1728 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.034$
$\theta_{\max} = 29.6°$
$h = -36 \rightarrow 36$
$k = -10 \rightarrow 8$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.098$
$S = 1.06$
2806 reflections
173 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.092P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0030 (7)

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.4439 (13)	N1—C8	1.3421 (17)
S1—O2	1.4566 (13)	N1—C7	1.374 (2)
S1—O3	1.4670 (12)	N2—C7	1.3297 (18)
S1—C1	1.7528 (16)	N3—C7	1.307 (2)
O4—C4	1.355 (2)	N4—C8	1.308 (3)
O1—S1—O2	112.78 (8)	C8—N1—C7	120.76 (15)
O1—S1—O3	112.37 (8)	C7—N2—C7$^{\text{i}}$	115.91 (18)
O2—S1—O3	110.00 (7)	N3—C7—N2	120.15 (15)
O1—S1—C1	106.74 (7)	N3—C7—N1	117.08 (15)
O2—S1—C1	107.55 (7)	N2—C7—N1	122.75 (14)
O3—S1—C1	107.07 (7)	N4—C8—N1	121.5 (1)
C5—C6—C1	120.14 (14)	N1$^{\text{i}}$—C8—N1	117.0 (2)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The positions of the H atoms of the melaminium residue and of the hydroxyl (OH) group of the *p*-hydroxybenzenesulfonate ion, as well as those of the water molecule, *i.e.* of all H atoms involved in hydrogen bonding, were refined. Other H atoms were treated as riding, with C—H = 0.93 Å. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{O})$.

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N1—H1N1$\cdots$O2$^{\text{i}}$	0.85 (2)	1.85 (2)	2.699 (2)	172 (2)
O4—H1O4$\cdots$O5	0.89 (3)	1.93 (3)	2.786 (2)	162 (2)
N3—H1N3$\cdots$O3$^{\text{ii}}$	0.86 (2)	2.12 (2)	2.945 (2)	162 (2)
N3—H2N3$\cdots$O5$^{\text{iii}}$	0.86 (2)	2.21 (2)	2.905 (2)	138 (2)
N4—H1N4$\cdots$O3$^{\text{i}}$	0.93 (2)	1.93 (2)	2.846 (2)	170 (2)
O5—H1O5$\cdots$O3$^{\text{iii}}$	0.93 (2)	2.10 (2)	2.997 (2)	163 (2)
O5—H2O5$\cdots$O1$^{\text{iv}}$	0.93 (2)	2.14 (2)	2.905 (2)	138 (2)

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

Data collection: *KM*-4 *CCD Software* (Kuma Diffraction, 1999); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1522). Services for accessing these data are described at the back of the journal.

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