

Bis(melaminium) DL-malate  
tetrahydrateJan Janczak<sup>a\*</sup> and Genivaldo Julio Perpétuo<sup>b</sup><sup>a</sup>Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland, and <sup>b</sup>Departamento de Física, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, CEP 35.400-000, Ouro Preto, MG, Brazil

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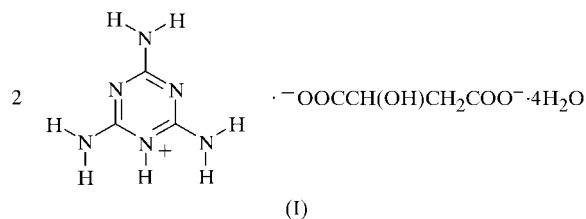
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The crystal structure of the title melaminium salt, bis(2,4,6-triamino-1,3,5-triazin-1-ium) DL-malate tetrahydrate,  $2\text{C}_3\text{H}_7\text{N}_6^+ \cdot \text{C}_4\text{H}_4\text{O}_5^{2-} \cdot 4\text{H}_2\text{O}$ , consists of singly protonated melaminium residues, DL-malate dianions and water molecules. The melaminium residues are connected into chains by four  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonds, and these chains form a stacking structure along the *c* axis. The DL-malate dianions form hydrogen-bonded chains and, together with hydrogen-bonded water molecules, form a layer parallel to the (100) plane. The conformation of the malate ion is compared with an *ab initio* molecular-orbital calculation. The oppositely charged moieties, *i.e.* the stacks of melaminium chains and hydrogen-bonded DL-malate anions and water molecules, form a three-dimensional polymeric structure, in which  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds stabilize the stacking.

## Comment

The present study is a continuation of our investigations characterizing the hydrogen bonds formed by triazine derivatives in the solid state (Janczak & Kubiak, 1999; Janczak & Perpétuo, 2001*a,b,c,d*; Janczak & Perpétuo, 2002*a,b*; Perpétuo & Janczak, 2002*a,b*). Melamine and its organic and inorganic complexes or salts can develop well defined supramolecular structures *via* multiple hydrogen bonds by self-assembly of components that contain complementary arrays of hydrogen-bonding sites (Desiraju, 1990; MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). To expand our understanding of the solid-state physical-organic chemistry of compounds containing multiple hydrogen-bonding systems, we present here the solid-state structure of the title compound, bis(2,4,6-triamino-1,3,5-triazin-1-ium) DL-malate tetrahydrate, (I). Additionally, the geometries of the oppositely charged parts, *i.e.* the singly protonated melaminium cation and the DL-malate dianion, are compared with *ab initio* fully optimized parameters calculated

at the HF/6-31G(d,p) level (Frisch *et al.*, 1995). The *ab initio* molecular-orbital calculations were carried out on isolated ions, and the results are illustrated in Fig. 1.



The asymmetric unit of (I) consists of two melaminium cations, singly protonated at one of the ring N atoms, a DL-malate dianion and four water molecules (Fig. 2). The six-membered rings of the singly protonated melaminium residues exhibit significant distortions from the ideal hexagonal form (Table 1). The internal C—N—C angle at the protonated N atom in both independent melaminium cations is greater than the other two C—N—C angles within the ring. This difference is a result of the steric effect of a lone-pair electron, as predicted by the valence-shell electron-pair repulsion theory (Gillespie, 1963, 1992). As a result of the protonation of the melamine ring at one of the three N atoms, the internal N—C—N angle involving only the non-protonated N atoms is significantly greater than the N—C—N angles involving both protonated and non-protonated N atoms. The *ab initio* opti-

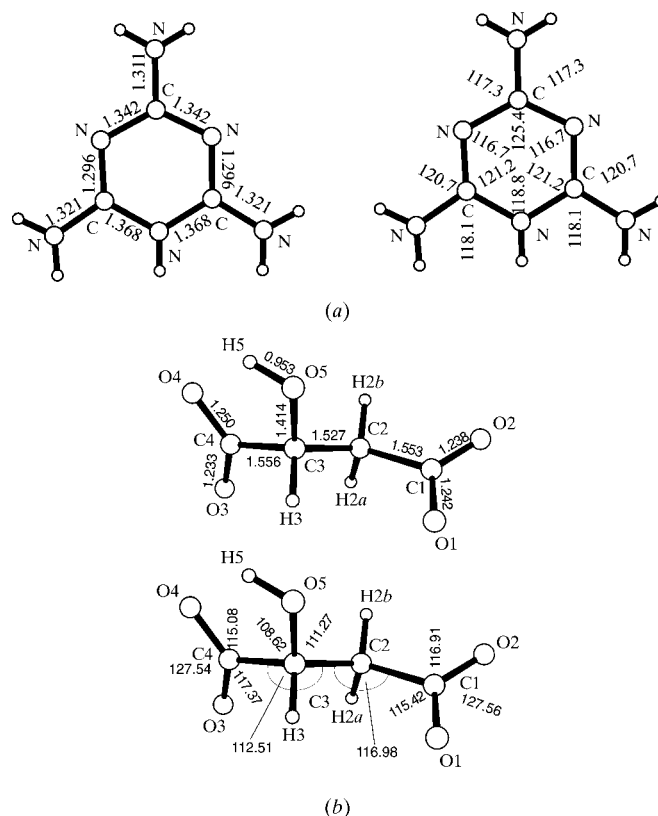
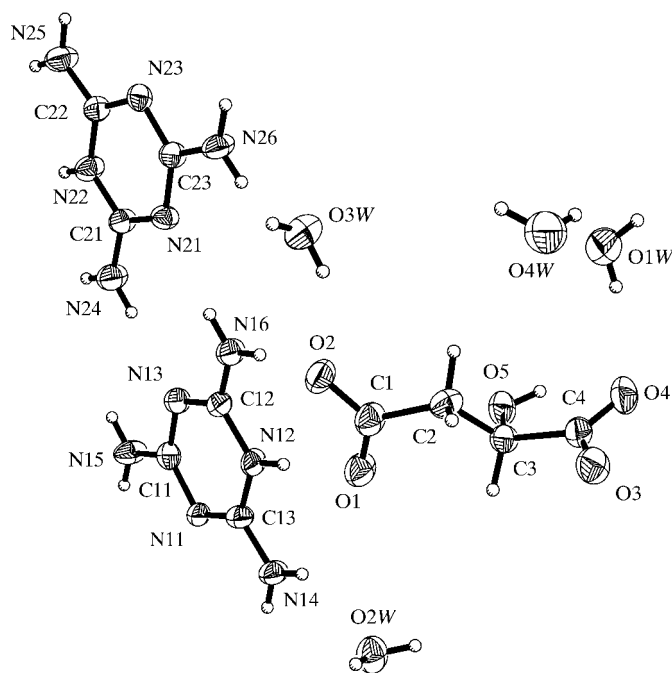


Figure 1

The results of the optimized molecular-orbital calculations (Å, °) for (a) the melaminium cation and (b) the malate(2<sup>-</sup>) ion.

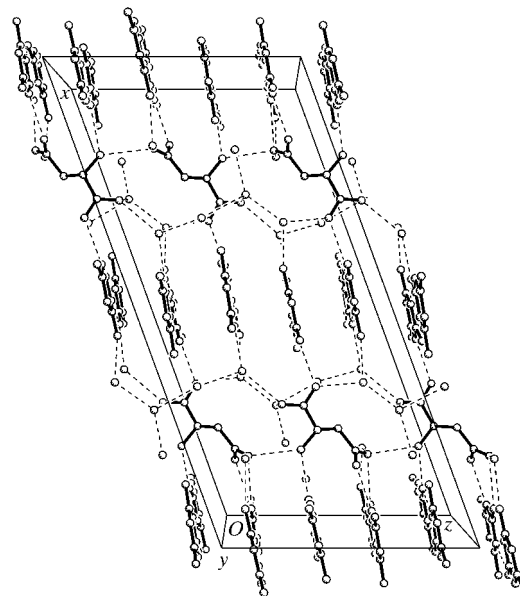
mized geometry calculated for the singly protonated melaminium residue shows a correlation between the C–N–C and N–C–N angles within the ring that is similar to the correlation seen in the crystal. Thus, the ring distortion of the singly protonated melaminium residue results mainly from the protonation and, to a lesser degree, from the hydrogen-bonding system and the crystal packing. The C–N bond lengths in the optimized melaminium residue are slightly shorter than those in the crystal. The lengthening of these C–N bonds in the crystal is likely to be due to the interaction of the  $\pi$ - $\pi$  clouds between the rings in the stacks and the hydrogen-bonding system. A similar correlation between the internal C–N–C and N–C–N angles within the melaminium ring is reported for crystals of barbituric acid with melamine (Zerkowski *et al.*, 1994), melaminium phthalate (Janczak & Perpétuo, 2001a), melaminium chloride hemihydrate (Janczak & Perpétuo, 2001c), bis(melaminium) sulfate dihydrate (Janczak & Perpétuo, 2001d), melaminium acetate (Perpétuo & Janczak, 2002a), melaminium glutarate monohydrate (Janczak & Perpétuo, 2002a) and melaminium phosphate (Janczak & Perpétuo, 2002b), *i.e.* those singly protonated melaminium salts that have been previously structurally characterized.

Each melaminium residue is involved in nine hydrogen bonds; in seven of these it acts as a donor and in the remaining two it acts as an acceptor. Two pairs of almost linear N–H $\cdots$ N hydrogen bonds link the melaminium moieties into chains, which in turn form stacks along the [001] direction. Within one stack, the melaminium residues are separated by 3.196 (3) Å. This distance is shorter than that between the  $\pi$ -aromatic ring systems (3.4 Å; Pauling, 1960) and indicates



**Figure 2**

A view of the molecular structure of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii.



**Figure 3**

A view of the crystal packing, showing the stacking structure of hydrogen-bonded melaminium residues that stabilize the N–H $\cdots$ O hydrogen bonds, and the layer of O–H $\cdots$ O hydrogen-bonded malate ions and water molecules. Dashed lines represent hydrogen bonds and H atoms have been omitted for clarity.

$\pi$ - $\pi$  interactions between the melaminium rings in the stack. The remaining five N–H $\cdots$ O hydrogen bonds (see Table 2), which are more bent, link the chains of melaminium residues with DL-malate ions and water molecules (see Fig. 3). These N–H $\cdots$ O hydrogen bonds stabilize the stacking structure. One of the melaminium moieties forms three hydrogen bonds with two malate ions (with atoms O1 and O2 of one malate ion and with atom O5 of the other malate ion), while the other melaminium residue forms only two hydrogen bonds with two malate ions (with atom O3 of one malate ion and with atom O5 of the second). Atom H12 on the protonated N atom of one melamine residue is involved in a hydrogen bond with atom O1 of the COO $^-$  group, while atom H22 on the protonated N atom of the second melaminium residue forms a hydrogen bond with atom O3 of the other COO $^-$  group. Additionally, the first melaminium residue is involved in hydrogen bonds with two water molecules (O2W and O4W), and the other melaminium cation is involved in hydrogen bonds with three water molecules (O2W, O3W and O4W).

The C1–C2–C3–C4 ( $\psi$ ), O4–C4–C3–O5 ( $\varphi_2$ ) and C3–C2–C1–O1 ( $\chi$ ) torsion angles describe well the conformation of the malate ion and the conformation of malic acid (Sluis & Kroon, 1985; 1989). The conformation of the carbon skeleton of the malate anion is extended [ $\psi = -170.5$  (3) $^\circ$ ], with the C3-carboxyl group almost coplanar with atoms C3 and O5 [ $\varphi_2 = 7.3$  (4) $^\circ$ ], because of the intramolecular O5–H5 $\cdots$ O4 hydrogen-bonding interaction, with a relatively short O5 $\cdots$ O4 distance. The conformation of the C2-carboxyl group (COO $^-$ ) around the C–C bond is clinal [ $\chi = 17.3$  (4) $^\circ$ ]. In the optimized malate dianion, the values of  $\psi$ ,  $\varphi_2$  and  $\chi$  are  $-166.3$ ,  $4.2$  and  $36.9^\circ$ , respectively. The

greatest difference between the angles in the optimized ion and those in the crystal malate ion is found for angle  $\chi$ , which describes the orientation of the  $\text{COO}^-$  group at atom C2; the difference results from the formation of relatively strong  $\text{O} \cdots \text{H} - \text{N}$  hydrogen bonds with the melaminium moiety. The optimized  $\text{O} - \text{C} - \text{O}$  angles in both dissociated carboxyl groups are greater than those in the crystal, probably because of the diminishing steric effect of lone pairs of electrons on the O atoms, due to the  $\text{O} \cdots \text{H} - \text{N}$  and  $\text{O} \cdots \text{H} - \text{O}$  hydrogen-bonding interactions. The  $\text{C} - \text{O}$  bonds in both  $\text{COO}^-$  groups are intermediate between single  $\text{Csp}^2 - \text{O}$  (1.308–1.320 Å) and double  $\text{Csp}^2 = \text{O}$  bonds (1.214–1.224 Å; Allen *et al.*, 1987; Allen, 2002) indicating delocalization of the charge on both O atoms of the  $\text{COO}^-$  groups. The slight differences between the  $\text{C1} - \text{O1}$  and  $\text{C1} - \text{O2}$  bonds in one  $\text{COO}^-$  group, and between the  $\text{C4} - \text{O3}$  and  $\text{C4} - \text{O4}$  bonds in the other  $\text{COO}^-$  group, correlate well with the strength of the hydrogen bonds in which the O atoms are involved (Table 2). The  $\text{C3} - \text{O5}$  bond length is slightly longer in the crystal than in the *ab initio* calculation, since, in the crystal, the hydroxyl group is involved in four hydrogen bonds, *viz.* in two as a donor and in two as an acceptor. Thus, hydroxyl atom H5 of the malate ion forms a bifurcated hydrogen bond. The malate ions form hydrogen-bonded chains *via*  $\text{O5} - \text{H5} \cdots \text{O2}(x, 2 - y, z - \frac{1}{2})$  interactions and, together with hydrogen-bonded water molecules, form a two-dimensional layer parallel to the (100) plane.

Two pairs of water molecules ( $\text{O1W}$  and  $\text{O4W}$ ) related by an inversion centre form a hydrogen-bonded cyclic tetramer in which atom  $\text{O4W}$  is a donor and atom  $\text{O1W}$  is an acceptor. Additionally, water molecule  $\text{O3W}$  interacts as an acceptor with atom  $\text{H21W}$ , and water molecule  $\text{O2W}$  interacts *via* atom  $\text{H22W}$  to form an  $\text{O2W} - \text{H22W} \cdots \text{O4W}(\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$  hydrogen bond.

## Experimental

Melamine was added to a solution of DL-malic acid (10%) and the resulting solution was evaporated slowly. After several days, colourless crystals of (I) appeared.

### Crystal data

$2\text{C}_3\text{H}_7\text{N}_6^+ \cdot \text{C}_4\text{H}_4\text{O}_5^{2-} \cdot 4\text{H}_2\text{O}$   
 $M_r = 458.43$   
 Monoclinic,  $C2/c$   
 $a = 26.533$  (5) Å  
 $b = 12.297$  (2) Å  
 $c = 13.079$  (3) Å  
 $\beta = 110.00$  (3)°  
 $V = 4010.0$  (16) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.519$  Mg m<sup>-3</sup>  
 $D_m = 1.52$  Mg m<sup>-3</sup>

$D_m$  measured by flotation in dichloroethane/dibromoethane  
 Mo  $K\alpha$  radiation  
 Cell parameters from 3878 reflections  
 $\theta = 3.2 - 28.4^\circ$   
 $\mu = 0.13$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Parallelepiped, colourless  
 $0.28 \times 0.24 \times 0.16$  mm

### Data collection

Kuma KM-4 area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990)  
 $T_{\min} = 0.961$ ,  $T_{\max} = 0.968$   
 15 560 measured reflections

4986 independent reflections  
 3878 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 28.4^\circ$   
 $h = -24 \rightarrow 35$   
 $k = -16 \rightarrow 16$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.041$   
 $S = 1.07$   
 4986 reflections  
 305 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0061P)^2 + 0.0402P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.009$   
 $\Delta\rho_{\text{max}} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.28$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.000227 (7)

**Table 1**

Selected geometric parameters (Å, °).

N11—C13	1.312 (3)	N23—C22	1.340 (3)
N11—C11	1.368 (3)	N23—C23	1.351 (3)
N12—C12	1.357 (3)	O1—C1	1.243 (3)
N12—C13	1.359 (3)	O2—C1	1.261 (3)
N13—C11	1.339 (3)	C1—C2	1.516 (3)
N13—C12	1.343 (3)	C2—C3	1.521 (3)
N21—C23	1.326 (3)	C3—O5	1.426 (2)
N21—C21	1.341 (3)	C3—C4	1.501 (3)
N22—C21	1.341 (3)	C4—O4	1.236 (3)
N22—C22	1.345 (3)	C4—O3	1.269 (3)
C13—N11—C11	115.5 (2)	N21—C23—N23	127.9 (2)
C12—N12—C13	118.8 (2)	O1—C1—O2	122.9 (3)
C11—N13—C12	116.0 (2)	O1—C1—C2	119.7 (3)
N13—C11—N11	125.5 (2)	O2—C1—C2	117.4 (3)
N13—C12—N12	121.4 (3)	C1—C2—C3	114.1 (2)
N11—C13—N12	122.8 (3)	O5—C3—C4	110.9 (2)
C23—N21—C21	114.7 (2)	O5—C3—C2	109.7 (2)
C21—N22—C22	119.1 (2)	C4—C3—C2	111.1 (2)
C22—N23—C23	113.5 (2)	O4—C4—O3	122.5 (3)
N21—C21—N22	122.0 (3)	O4—C4—C3	120.0 (3)
N23—C22—N22	122.7 (3)	O3—C4—C3	117.5 (3)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D - H \cdots A$	$D - H$	$H \cdots A$	$D \cdots A$	$D - H \cdots A$
N12—H12 <sup>i</sup> ···O1	0.86	1.79	2.635 (3)	169
N14—H14A···N23 <sup>i</sup>	0.86	2.09	2.950 (3)	179
N14—H14B···O2W	0.86	2.21	2.890 (3)	136
N15—H15A···O5 <sup>ii</sup>	0.86	2.14	2.977 (3)	165
N15—H15B···O4W <sup>iii</sup>	0.86	2.28	3.085 (3)	156
N16—H16A···N21	0.86	2.19	3.045 (3)	175
N16—H16B···O2	0.86	2.00	2.851 (3)	170
N22—H22···O3 <sup>iv</sup>	0.86	1.82	2.656 (3)	164
N24—H24A···N13	0.86	2.06	2.920 (3)	174
N24—H24B···O5 <sup>ii</sup>	0.86	2.25	2.950 (3)	139
N25—H25A···N11 <sup>v</sup>	0.86	2.19	3.046 (3)	176
N25—H25B···O4W <sup>iv</sup>	0.86	2.47	3.091 (3)	129
N26—H26A···O3W	0.86	2.19	2.956 (3)	148
N26—H26B···O2W <sup>v</sup>	0.86	2.18	3.008 (3)	162
O5—H5···O4	0.82	2.16	2.646 (3)	118
O5—H5···O2 <sup>vi</sup>	0.82	2.24	2.919 (3)	141
O1W—H11W···O4	0.85	1.98	2.801 (3)	162
O1W—H21W···O3W <sup>vii</sup>	0.85	1.89	2.728 (3)	170
O2W—H12W···O4 <sup>viii</sup>	0.85	1.97	2.815 (3)	170
O2W—H22W···O4W <sup>ix</sup>	0.85	2.11	2.908 (3)	156
O3W—H13W···O2	0.85	1.86	2.702 (3)	170
O3W—H23W···O3 <sup>x</sup>	0.85	1.96	2.778 (3)	161
O4W—H14W···O1W	0.85	2.02	2.763 (3)	145
O4W—H24W···O1W <sup>xi</sup>	0.85	2.32	2.836 (3)	119

Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $1 - x, 2 - y, -z$ ; (iii)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (iv)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (v)  $x, 1 + y, z$ ; (vi)  $x, 2 - y, z - \frac{1}{2}$ ; (vii)  $\frac{3}{2} - x, \frac{3}{2} - y, -z$ ; (viii)  $\frac{3}{2} - x, \frac{3}{2} - y, -z$ ; (ix)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (x)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

Data collection: *KM-4 Software* (Kuma, 2000); cell refinement: *KM-4 Software*; data reduction: *KM-4 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: NA1613). Services for accessing these data are described at the back of the journal.

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