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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Melaminium Diperchlorate Hydrate

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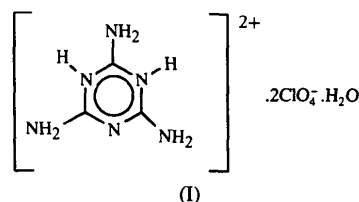
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Abstract

The structure of the new melaminium salt, 2,4,6-triamino-1,3,5-triazine-1,3-dium diperchlorate hydrate, $C_7H_9N_4S^+ \cdot 2ClO_4^- \cdot H_2O$, has been characterized using low-temperature X-ray diffraction data (100 K). Melaminium diperchlorate has a high density ($\rho_c = 1.94 \text{ Mg m}^{-3}$), is extensively hydrogen bonded and contains a water dimer.

Comment

The asymmetric unit of melaminium diperchlorate, (I), consists of two well defined perchlorate anions, a well defined aromatic ring protonated at two of the three ring N atoms and a partially disordered water molecule.



There is an extensive hydrogen-bonding network throughout the lattice (Fig. 1). Both perchlorate anions have the expected tetrahedral geometry, with bond lengths ranging from 1.430 (2) (Cl1—O1) to 1.458 (1) Å (Cl1—O4). The bond angles range from 108.78 (7) (O3—Cl1—O4) to 110.86 (8)° (O6—Cl2—O7). Protonation of the ring N atoms distorts the bond lengths in the aromatic ring. The two shortest bonds [N3—C3 1.320 (2) and N3—C1 1.333 (2) Å] are those furthest from the protonated ring N atoms. The two longest bonds [N2—C3 1.378 (2) and N1—C1 1.376 (2) Å] are those connected to the shortest bonds. This has the effect of opening up the ring bond angles at atoms C1 and C3, thus creating the largest bond angles in the ring [N2—C3—N3 122.2 (2) and N1—C1—N3 122.1 (1)°]. The amine groups do not appear to be affected in any systematic way by the distortion of the ring.

The bond length most likely to be affected, N5—C2 [1.304 (2) Å], lies midway between N4—

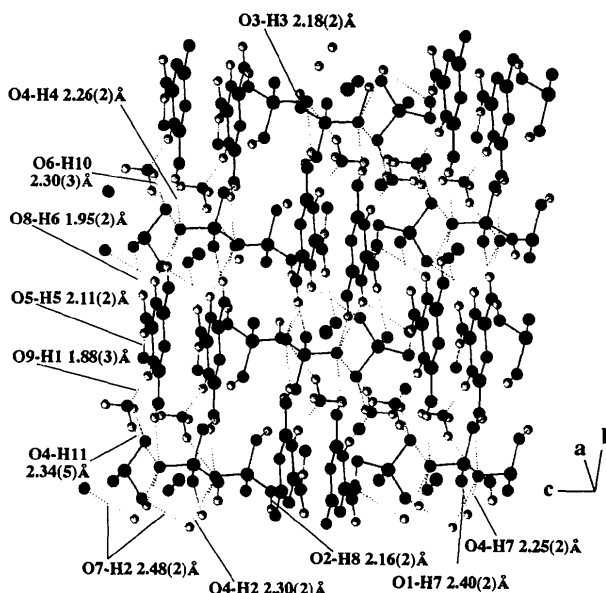


Fig. 1. Packing diagram for melaminium diperchlorate showing three unit cells in the *a* direction and two unit cells in the *b* and *c* directions, with hydrogen bonds ($O \cdots H < 2.5 \text{ Å}$) shown.

C1 [1.301 (2) Å] and N6—C3 [1.309 (2) Å]. A semi-empirical calculation, with the AM1 parameter set (Dewar, Zoebisch, Healy & Stewart, 1985), on the protonated melaminium dication results in the same geometrical features. Thus, the ring distortion is a result of protonation and not hydrogen bonding or crystal packing. The distortion of the aromatic ring is quite similar to that reported for the melamine–cyanuric acid complex hydrochloride (Wang, Wei & Wang, 1990), the only other simple salt of diprotonated melamine that has been structurally determined.

For the purposes of this discussion a hydrogen bond has been defined as having an O···H contact of less than 2.5 Å.

One perchlorate anion (Fig. 2) is involved in seven or eight hydrogen bonds, depending on the orientation of the disordered water molecule. These bonds come from four different melaminium moieties. Atom O4 is the most interesting as it accepts three hydrogen bonds. These are O4···H4 [2.26 (2) Å], O4···H7 [2.25 (2) Å] and O4···H2 [2.30 (2) Å]. It also forms a hydrogen bond with a half-occupied H atom on the water molecule, O4···H11 [2.34 (5) Å]. Each of the other O atoms has one H atom bonded to it. The shortest of all the hydrogen bonds to this perchlorate anion is O2···H8 [2.16 (2) Å], which is almost linear [O2···H8—N6 168 (2)°]. The longest is O1···H7 [2.40 (2) Å], which is substantially bent [O1···H7—N6 110 (2)°].

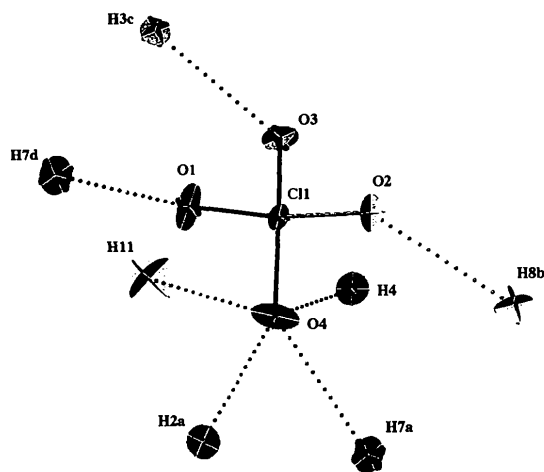


Fig. 2. Diagram with 50% displacement ellipsoids showing the hydrogen bonds to perchlorate (1) [symmetry codes: (a) $x, y + 1, z$; (b) $-x + 2, -y + 1, -z + 1$; (c) $x - 1, y, z$; (d) $x - 1, y + 1, z$].

The other perchlorate anion (Fig. 3) forms four hydrogen bonds with two different melaminium moieties. There is one hydrogen bond to each O atom. The shortest is O8···H6 [1.95 (2) Å], which is essentially linear [O8···H6—N5 173 (2)°], while the longest is O7···H2 [2.48 (2) Å], which is very bent [O7···H2—N2 114 (2)°].

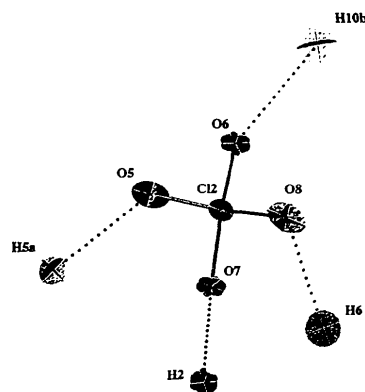


Fig. 3. Diagram with 50% displacement ellipsoids showing the hydrogen bonds to perchlorate (2) [symmetry codes: (a) $-x, -y, -z$; (b) $x, y - 1, z$].

The melaminium moiety (Fig. 4) has 11 O atoms bonded to it from both perchlorate anions, related by one of six different symmetry operations. The most noticeable feature is that there are two bifurcated hydrogen bonds (involving atoms H2 and H7) and that they share a common O atom (O4). Both H2 and H7 have the shorter of their bifurcated bonds to O4 [O4···H2 2.30 (2) and O4···H7 2.25 (2) Å], with very similar bond angles [O4···H2—N2 142 (2) and O4···H7—N6 143 (2)°]. The second bond from each H atom is longer [O7···H2 2.48 (2) and O1···H7 2.40 (2) Å] and is bent even more [O7···H2—N2 114 (2) and O1···H7—N6 110 (2)°]. These bonds are clearly of a weaker nature. The remainder of the hydrogen bonding involving the melaminium cation is quite ordinary.

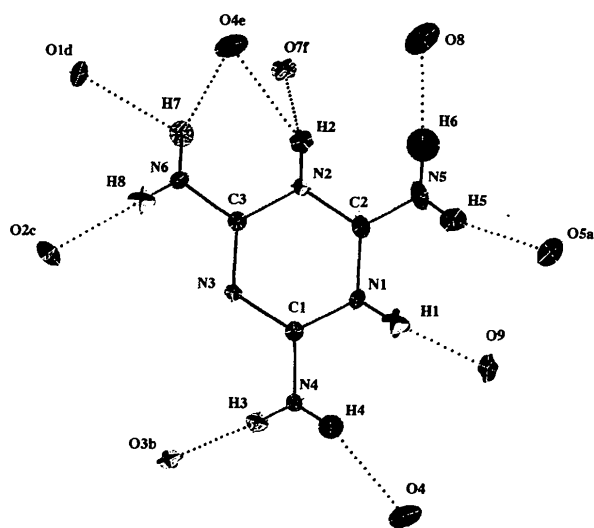
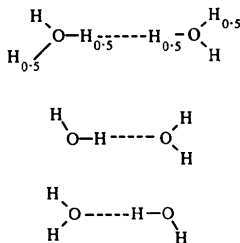


Fig. 4. Diagram with 50% displacement ellipsoids showing the hydrogen bonds from the melaminium cation [symmetry codes: (a) $-x, -y, -z$; (b) $x + 1, y, z$; (c) $-x + 2, -y + 1, -z + 1$; (d) $x + 1, y - 1, z$; (e) $x, y - 1, z$; (f) $x + 1, y, z$].

The disordered water molecule (Fig. 5) forms a hydrogen-bonded dimeric structure with itself across a center of symmetry and has the shortest hydrogen bonds in the crystal structure associated with it.



One orientation is H9—O9—H10 which forms a 'dimer' with the other orientation H10—O9—H11. The hydrogen bond H10—O9···H9 is 2.01 (4) Å long and has a bond angle of 108 (4)°. The shortest hydrogen bond in the crystal [O9···H1 1.88 (3) Å], between the water O atom and a melamineium H atom, is the same regardless of the orientation of the water molecule and is almost linear [O9···H1—N1 170 (2)°].

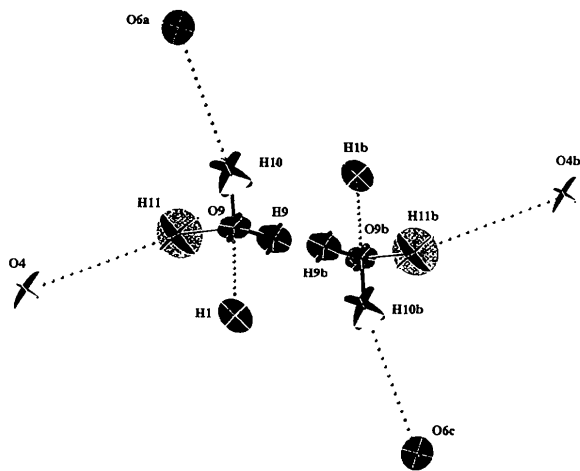


Fig. 5. Diagram with 50% displacement ellipsoids showing the hydrogen bonds to and from the water dimer [symmetry codes: (a) $x, y + 1, z$; (b) $-x + 1, -y + 1, -z$; (c) $-x + 1, -y + 2, -z$]. Atoms H9 and H11 are disordered with occupancies of 0.5.

Experimental

Melamine was dissolved in perchloric acid (60%) and the resulting solution was slowly evaporated. After several days, colorless crystals of the title salt appeared.

Crystal data

C₃H₈N₆²⁺·2ClO₄⁻·H₂O
 $M_r = 345.06$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Triclinic
 $P\bar{1}$
 $a = 5.8981 (6) \text{ \AA}$
 $b = 9.235 (1) \text{ \AA}$
 $c = 11.101 (2) \text{ \AA}$
 $\alpha = 97.85 (1)^\circ$
 $\beta = 90.38 (1)^\circ$
 $\gamma = 98.87 (1)^\circ$
 $V = 591.6 (3) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.94 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 ψ scans (North, Phillips
 & Mathews, 1968)
 $T_{\min} = 0.929$, $T_{\max} =$
 0.999
 2624 measured reflections
 2316 independent reflections

Refinement

Refinement on F
 $R = 0.026$
 $wR = 0.035$
 $S = 3.350$
 2180 reflections
 226 parameters
 All H-atom parameters
 refined
 $w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\max} = 0.002$

Cell parameters from 25
 reflections
 $\theta = 10\text{--}14^\circ$
 $\mu = 0.606 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Parallelepiped
 $0.31 \times 0.24 \times 0.20 \text{ mm}$
 Colorless

2180 observed reflections
 $[I > 3\sigma(I)]$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 25.99^\circ$
 $h = 0 \rightarrow 7$
 $k = -11 \rightarrow 11$
 $l = -13 \rightarrow 13$
 3 standard reflections
 frequency: 50 min
 intensity decay: 3.11%

$\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e \AA}^{-3}$
 Extinction correction:
 isotropic (Zachariasen,
 1963)
 Extinction coefficient:
 $0.13 (1) \times 10^{-4}$
 Atomic scattering factors
 from *International Tables*
 for X-ray Crystallography
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for H atoms; $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ for others.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
C11	0.46207 (6)	0.75853 (4)	0.40263 (3)	0.01158 (8)
C12	0.04855 (7)	-0.23629 (4)	0.04972 (3)	0.01499 (8)
O1	0.2716 (2)	0.8215 (1)	0.3642 (1)	0.0258 (3)
O2	0.5504 (2)	0.8351 (1)	0.5184 (1)	0.0225 (3)
O3	0.3927 (2)	0.6041 (1)	0.4101 (1)	0.0193 (3)
O4	0.6417 (2)	0.7739 (1)	0.3136 (1)	0.0240 (3)
O5	-0.0103 (3)	-0.2759 (2)	-0.0787 (1)	0.0342 (4)
O6	-0.0048 (2)	-0.3643 (1)	0.1097 (1)	0.0215 (3)
O7	-0.0784 (2)	-0.1222 (1)	0.0993 (1)	0.0201 (3)
O8	0.2909 (2)	-0.1812 (2)	0.0634 (2)	0.0360 (4)
O9	0.4262 (2)	0.5030 (1)	0.1226 (1)	0.0257 (3)
N1	0.6257 (2)	0.3266 (1)	0.2522 (1)	0.0140 (3)
N2	0.6880 (2)	0.0872 (1)	0.2558 (1)	0.0139 (3)
N3	0.9526 (2)	0.2837 (1)	0.3590 (1)	0.0123 (3)
N4	0.8955 (2)	0.5183 (1)	0.3420 (1)	0.0155 (3)
N5	0.3698 (3)	0.1308 (2)	0.1540 (1)	0.0214 (4)
N6	0.9965 (2)	0.0436 (1)	0.3649 (1)	0.0164 (3)
C1	0.8273 (3)	0.3763 (2)	0.3184 (1)	0.0117 (3)
C2	0.5570 (3)	0.1812 (2)	0.2192 (1)	0.0141 (4)
C3	0.8817 (3)	0.1407 (2)	0.3279 (1)	0.0123 (3)
H1	0.558 (4)	0.386 (2)	0.220 (2)	0.031 (6)
H2	0.650 (4)	-0.006 (2)	0.237 (2)	0.021 (5)
H3	1.022 (3)	0.548 (2)	0.377 (2)	0.018 (5)
H4	0.824 (4)	0.576 (2)	0.317 (2)	0.022 (5)
H5	0.297 (4)	0.189 (2)	0.136 (2)	0.026 (6)

H6	0.330 (4)	0.029 (3)	0.125 (2)	0.040 (7)
H7	0.954 (4)	-0.050 (2)	0.344 (2)	0.025 (6)
H8	1.111 (4)	0.075 (2)	0.406 (2)	0.027 (6)
H9†	0.474 (8)	0.498 (5)	0.050 (4)	0.03 (1)
H10	0.299 (4)	0.509 (3)	0.120 (2)	0.048 (8)
H11†	0.47 (1)	0.595 (6)	0.156 (5)	0.06 (2)

† Occupancy = 0.5.

Table 2. Selected geometric parameters (Å, °)

C1—O1	1.430 (1)	N1—C2	1.341 (2)
C1—O2	1.433 (1)	N2—C2	1.347 (2)
C1—O3	1.436 (1)	N2—C3	1.378 (2)
C1—O4	1.458 (1)	N3—C1	1.333 (2)
C2—O5	1.449 (1)	N3—C3	1.320 (2)
C2—O6	1.430 (1)	N4—C1	1.301 (2)
C2—O7	1.437 (1)	N5—C2	1.304 (2)
C2—O8	1.441 (1)	N6—C3	1.309 (2)
N1—C1	1.376 (2)		
O1—C11—O2	109.89 (8)	C1—N1—C2	120.3 (1)
O1—C11—O3	110.11 (7)	C2—N2—C3	120.2 (1)
O1—C11—O4	108.85 (8)	C1—N3—C3	117.2 (1)
O2—C11—O3	110.19 (8)	N1—C1—N3	122.1 (1)
O2—C11—O4	109.00 (7)	N1—C1—N4	118.4 (2)
O3—C11—O4	108.78 (7)	N3—C1—N4	119.5 (1)
O5—C12—O6	109.36 (8)	N1—C2—N2	117.9 (1)
O5—C12—O7	108.77 (9)	N1—C2—N5	121.7 (2)
O5—C12—O8	108.7 (1)	N2—C2—N5	120.4 (2)
O6—C12—O7	110.86 (8)	N2—C3—N3	122.2 (2)
O6—C12—O8	109.64 (9)	N2—C3—N6	117.4 (1)
O7—C12—O8	109.43 (8)	N3—C3—N6	120.4 (1)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O9	0.84 (3)	1.88 (3)	2.705 (2)	170 (2)
N2—H2...O4 ⁱ	0.85 (2)	2.30 (2)	3.021 (2)	142 (2)
N2—H2...O7 ⁱⁱ	0.85 (2)	2.48 (2)	2.931 (2)	114 (2)
N4—H3...O3 ⁱⁱⁱ	0.83 (2)	2.18 (2)	2.982 (2)	162 (2)
N4—H4...O4	0.80 (2)	2.26 (2)	3.033 (2)	161 (2)
N5—H5...O5 ⁱⁱⁱ	0.78 (2)	2.11 (2)	2.854 (2)	159 (2)
N5—H6...O8	0.94 (2)	1.95 (2)	2.884 (2)	173 (2)
N6—H7...O1 ^{iv}	0.86 (2)	2.40 (2)	2.804 (2)	110 (2)
N6—H7...O4 ⁱ	0.86 (2)	2.25 (2)	2.983 (2)	143 (2)
N6—H8...O2 ^v	0.81 (2)	2.16 (2)	2.951 (2)	168 (2)
O9—H9...O9 ^{vi}	0.85 (4)	2.01 (4)	2.860 (2)	176 (5)
O9—H10...O6 ^{vii}	0.76 (3)	2.30 (3)	2.998 (2)	153 (3)
O9—H11...O4	0.88 (5)	2.34 (5)	3.146 (2)	152 (5)

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

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The structure was solved by Patterson and Fourier methods.

Data collection: CAD-4 diffractometer software (Enraf-Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN PROCESS* (Fair, 1990) and *SORTAV* (Blessing, 1987). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *CACHE WORKSYSTEM* (Cache Scientific, 1993). Software used to prepare material for publication: *MolEN CIF VAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,8-Dimethyl-2-(3-furoylaminomethyl)-5-phenyl-2,3-dihydro-1H-1,4-benzodiazepin-4-ium Chloride

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Abstract

The diazepine ring of the title compound, $C_{23}H_{24}N_3O_2^+ \cdot Cl^-$, adopts a conformation halfway between a distorted boat and a distorted sofa. The furoylaminomethyl side chain is in an extended conformation placing the furan ring nearly parallel to the benzo part of the benzodiazepine ring. Two intramolecular hydrogen bonds to the Cl^- anion stabilize the observed conformation.

Comment

As part of a structure-activity study on a series of 2-acylaminomethylbenzodiazepine derivatives with opioid activity, the crystal structure of the title compound, (I), has been determined.

Compared to the five other structures of the series determined previously (Peeters, Blaton, Meurisse & De Ranter, 1994a,b, and references cited therein), the title structure does not show any unexpected features. The seven-membered ring is in the usual conformation halfway between a distorted boat and a distorted sofa