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Bis(2,4-diamino-6-oxopyrimidinium) sulfate monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.075
wR factor = 0.251
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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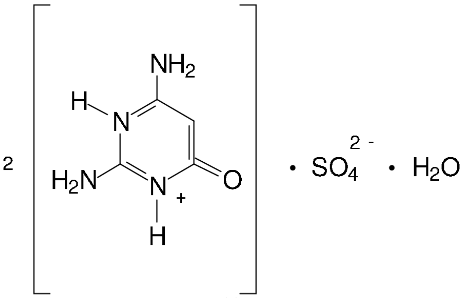
In the title compound, $C_4H_7N_4O^{2+}\cdot SO_4^{2-}\cdot H_2O$, the asymmetric unit contains two aminopyrimidinium cations, a sulfate anion and a water molecule. These species are connected by N—H⋯O and O—H⋯O hydrogen bonds, resulting in a three-dimensional network.

Comment

The crystal structure of the title compound, (I), has been determined as part of our ongoing studies of hydrogen-bonding interactions in protonated diaminopyrimidinium systems (Muthiah *et al.*, 2001).


(I)

The asymmetric unit of (I) contains two 2,4-diamino-6-oxopyrimidinium cations, a sulfate anion and a water molecule (Fig. 1). The tetrahedral sulfate ion has typical S—O distances [1.468 (3)–1.490 (4) Å] and O—S—O angles [107.9 (2)–111.6 (3)°]. Both the 2,4-diamino-6-oxopyrimidinium cations are protonated at the N1 position of the pyrimidine ring (Fig. 1), with internal ring angles of 122.8 (4) and 123.3 (4)° for C2—N1—C6 and C2′—N1′—C6′, respectively.

The sulfate ions and water molecules form a hydrogen-bonded chain by way of O—H⋯O bonds (Fig. 2 and Table 1). This type of interaction has also been observed in the crystal structure of bis(2,4-diaminopyrimidinium) sulfate monohydrate (Gomes *et al.*, 1996).

The sulfate anion interacts with the protonated N1 atom and the 2-amino group of the pyrimidine moiety through a pair of N—H⋯O hydrogen bonds (Table 1), forming a fork-like interaction. This can be designated by the graph-set notation $R_2^2(8)$ (Bernstein *et al.*, 1995). This motif is reminiscent of the cyclic hydrogen-bonded motif occurring in the crystal structures of many aminopyrimidine carboxylates (Allen *et al.*, 1998; Raj *et al.*, 2003). Adjacent N1-containing pyrimidinium cations are linked together by way of N—H⋯O bonds from the N3 and N4 amino donors to the O6^{v} keto acceptor (see Table 1 for symmetry code), resulting in chains containing $R_2^1(6)$ rings (Bernstein *et al.*, 1995). The N1′ pyri-

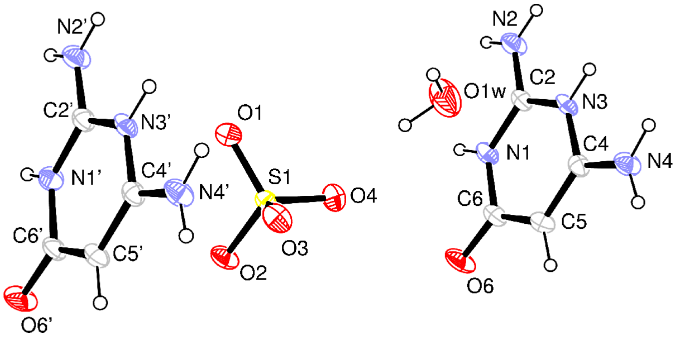


Figure 1
View of (I), showing 50% probability displacement ellipsoids (small spheres for the H atoms).

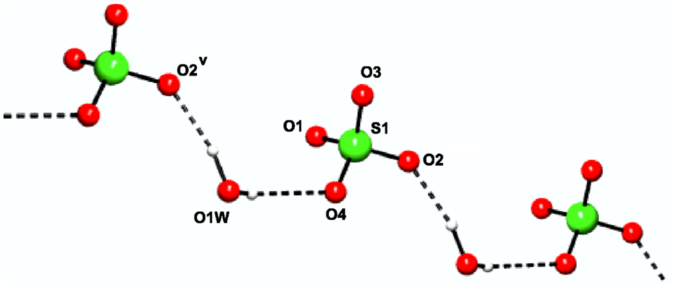


Figure 2
Detail of (I), showing a hydrogen-bonded chain of sulfate anions and water molecules [symmetry code: (v) $x, 1 + y, z$].

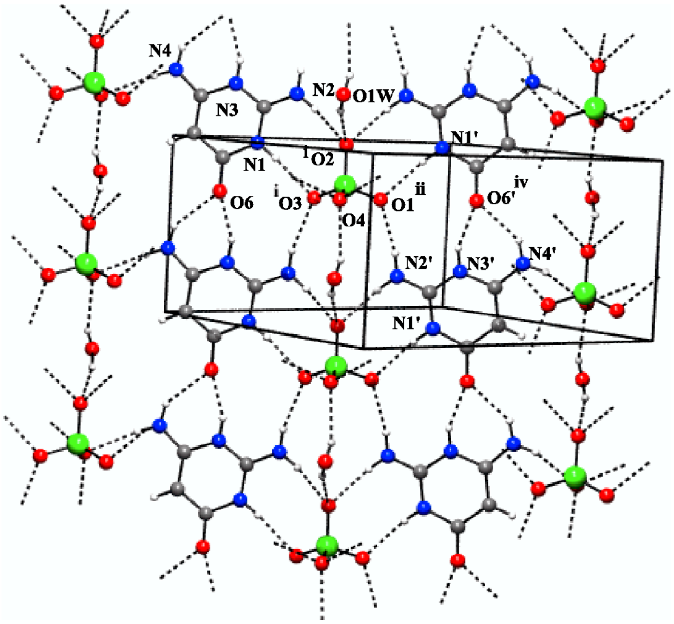


Figure 3
Hydrogen-bonding interactions in (I) shown as dashed lines [symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, -y, 1 - z$; (iv) $x, 1 + y, z$].

midinium cation forms similar chains, with cross-linking between the N1 and N1′ chains mediated by the water/sulfate chains (Fig. 3).

Experimental

To an aqueous methanol solution of 2,4-diamino-6-hydroxypyrimidine (62 mg, Aldrich) were added a few drops of sulfuric acid. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Crystals appeared from the mother liquor after a few days.

Crystal data

$2C_4H_7N_4O^+ \cdot O_4S^{2-} \cdot H_2O$
$M_r = 368.36$
Monoclinic, $P2_1/c$
$a = 15.014$ (3) Å
$b = 6.568$ (2) Å
$c = 15.330$ (3) Å
$\beta = 106.69$ (2)°
$V = 1448.0$ (6) Å^3
$Z = 4$
$D_x = 1.690$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 1.4$–25.6°
$\mu = 0.28$ mm^{-1}
$T = 293$ K
Block, colourless
0.37 × 0.29 × 0.22 mm

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: none
2811 measured reflections
2715 independent reflections
2210 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.102$
$\theta_{\rm max} = 25.6°$
$h = -18 \rightarrow 17$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 18$
1 standard reflection every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.075$
$wR(F^2) = 0.251$
$S = 1.13$
2715 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1166P)^2 + 5.4696P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.57$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.87$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3$^{\rm i}$	0.86	2.08	2.931 (6)	172
N1′—H1′···O1$^{\rm ii}$	0.86	2.06	2.914 (6)	170
N2′—H2A′···O2$^{\rm ii}$	0.86	2.02	2.836 (6)	158
O1W—H1W···O4	0.96	1.98	2.916 (7)	166
N2′—H2B′···O1$^{\rm iii}$	0.86	2.02	2.865 (6)	169
N2—H2A···O2$^{\rm i}$	0.86	1.98	2.794 (6)	158
N2—H2B···O3$^{\rm iv}$	0.86	2.11	2.945 (6)	165
O1W—H2W···O2$^{\rm v}$	0.97	1.97	2.906 (7)	164
N3—H3···O6$^{\rm v}$	0.86	1.83	2.638 (6)	156
N3′—H3′···O6′$^{\rm v}$	0.86	1.85	2.648 (5)	153
N4—H4A···O6$^{\rm v}$	0.86	2.16	2.883 (6)	142
N4—H4B···O4$^{\rm vi}$	0.86	2.16	2.935 (6)	149
N4′—H41′···O4$^{\rm vii}$	0.86	2.15	2.925 (6)	150
N4′—H42′···O6′$^{\rm v}$	0.86	2.10	2.831 (6)	143

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

The H atoms of the water molecule were located in a difference map and refined as riding in their as-found relative positions. The other H atoms were placed in idealized locations (C—H = 0.93 Å and N—H = 0.86 Å) and refined as riding. The constraint $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom) was applied in all cases.

Data collection: *FEBO* (Belletti, 1996); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2004); software used to prepare material for publication: *PLATON*.

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