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Influence of anion substitution on hydrogen-bonding patterns of salt compounds: cytosinium hydrogen sulfate and cytosinium perchlorate

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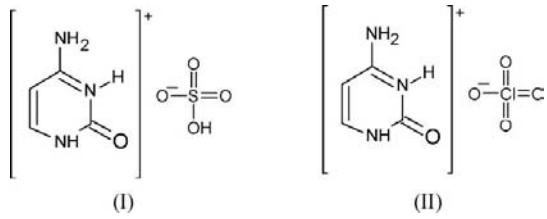
In the two title compounds, cytosinium hydrogen sulfate, $C_4H_6N_3O^+\cdot HSO_4^-$, (I), and cytosinium perchlorate, $C_4H_6N_3O^+\cdot ClO_4^-$, (II), the asymmetric units comprise a cytosinium cation with hydrogen sulfate and perchlorate anions, respectively. The crystal structures of (I) and (II) are similar; that of (I) is characterized by a three-dimensional N—H···O, O—H···O and C—H···O hydrogen-bonded network. In (I) and (II), two-dimensional layers are formed by N—H···O and C—H···O hydrogen bonds and, in the case of (I), they are linked by O—H···O hydrogen bonds where the anion acts as a donor and the cation as an acceptor. The hydrogen-bonded sheets in (II) form an angle of 87.1°.

Comment

The present work is part of a general structural study of purine and pyrimidine base salt compounds and their hydrogen-bonding patterns. A series of similar compounds has been reported previously, *viz*. cytosinium nitrate (Cherouana, Bouchouit *et al.*, 2003), adeninium perchlorate (Bendjeddou *et al.*, 2003), guaninium sulfate (Cherouana, Benali-Cherif *et al.*, 2003) and cytosinium oxalate monohydrate (Bouchouit *et al.*, 2005).

Hydrogen bonding dominates the formation of secondary structure in proteins, and its importance in the structure and function of biomolecules has been stressed by Jeffrey & Saenger (1991).

The nucleic acid base used in this study, *viz*. 6-amino-pyrimidine-2-one (cytosine), is one of the pyrimidine bases found in deoxyribonucleic acids and has been the subject of investigations aimed at studying the electrostatic properties of its monohydrate form (Weber & Craven, 1990). In our search for new salt compounds and as part of an investigation of the functionality of biological systems, we have prepared cytosinium hydrogen sulfate, (I), cytosinium perchlorate, (II), and cytosinium nitrate in order to study the important role that hydrogen bonding plays in these structures.



The crystal structure of cytosinium nitrate was reported by Cherouana, Bouchouit *et al.* (2003). It consists of parallel mixed cation–anion sheets stacked along [101]. These sheets feature moderate N—H···O and weak C—H···O hydrogen bonds with dominant $R_d^a(n)$ graph sets (Bernstein *et al.*, 1995). Interaction between sheets is facilitated by van der Waals interactions.

In both (I) and (II), the organic part is in its cationic form. As observed in all structures containing this cation (Kindberg & Amma, 1975), the cytosine is mono-protonated at N3 and this is clearly evidenced by the bond-length and valence-angle variations involving atom N3 (Table 1). Bond lengths in the tetrahedral hydrogen sulfate group also indicate the position of the H atom. There are three short S—O bonds of

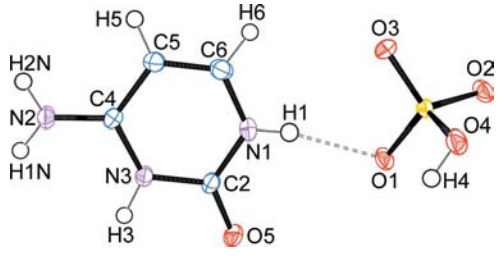


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the hydrogen bond.

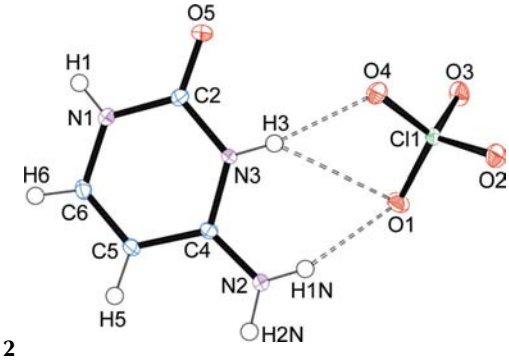


Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the hydrogen bonds.

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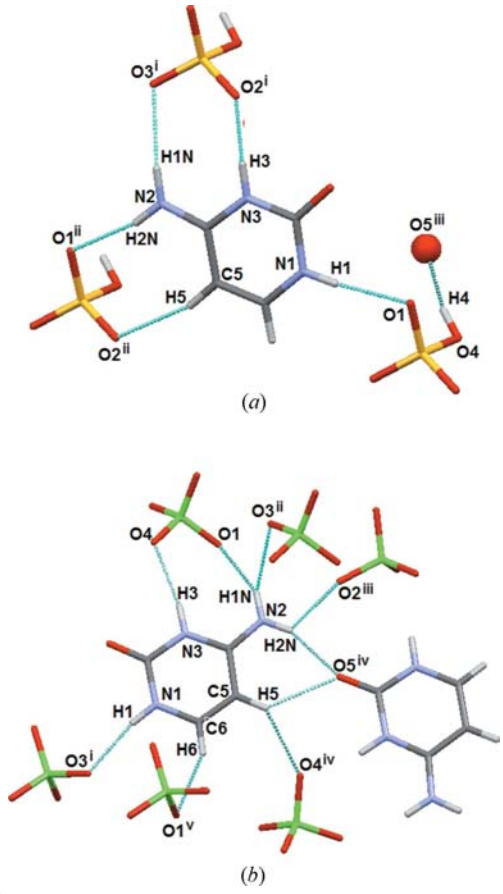

Figure 3
Hydrogen bonds (dashed lines) around the cytosinium cation in (*a*) (I) and (*b*) (II).

1.4608 (18), 1.458 (2) and 1.4530 (18) Å to terminal atoms O1, O2 and O3, respectively, and one longer bond of 1.556 (2) Å to atom O4, which is bound to atom H4. In perchlorate (II), the Cl atom is linked *via* four short bonds of 1.4454 (9), 1.4302 (9), 1.4509 (9) and 1.4533 (9) Å to terminal atoms O3, O4 O5 and O6, respectively, and this is consistent with the absence of an H atom in this anion. The asymmetric unit of (I) consists of a protonated cytosine ring and a hydrogen sulfate anion (Fig. 1), while that of (II) consists of a protonated cytosine ring and a perchlorate anion (Fig. 2).

Supramolecular aggregations in (I) and (II) are based on three-dimensional hydrogen-bonding networks that are dominated by N—H···O hydrogen bonds. Hence, the only unique hydrogen bonds observed are one O—H···O and one C—H···O in (I), and three C—H···O in (II) (Tables 2 and 3). It is noteworthy that hydrogen bonds between cytosinium rings (Fig. 3) are absent in (I), contrary to what was observed in cytosine (Barker & Marsh, 1964), cytosine monohydrate (Jeffrey & Kinoshita, 1963), cytosine hydrochloride (Mandel, 1977) and in the structure of (II) reported here. This is due to the presence of the hydrogen sulfate H atom, which separates the two cations by virtue of the anion-to-cation O—H···O hydrogen bond. The protonated cytosine rings are planar, with the greatest deviation from the least-squares plane being 0.043 (2) Å for the amino N atom in (I) and 0.077 (10) Å in (II). The amino H atoms also lie in this plane. The pyrimidine

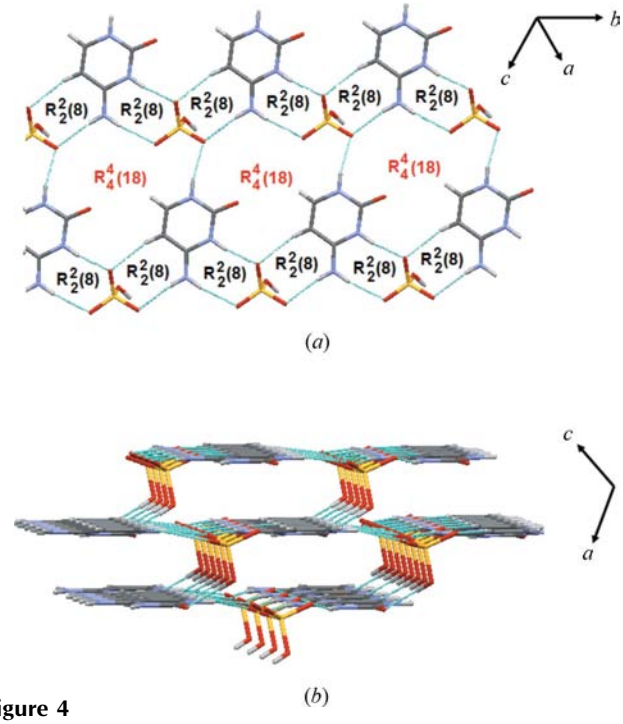

Figure 4
The hydrogen-bonding pattern in (I), showing (*a*) rings constructed from extended chains and (*b*) layers parallel to [102] generated by combination of the rings.

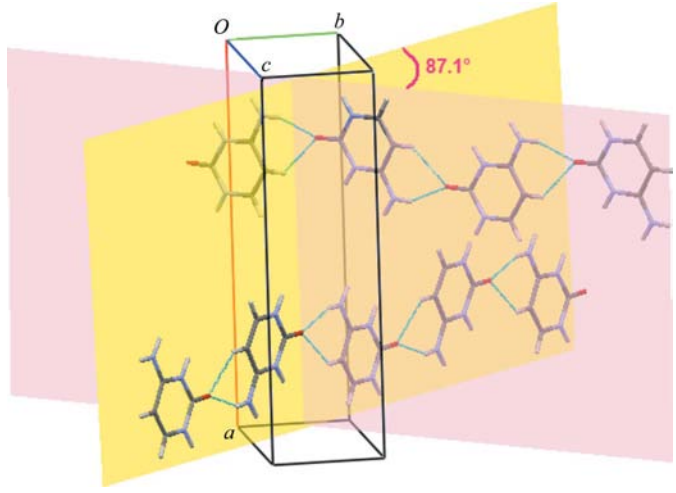

Figure 5
Cation–cation hydrogen-bonded chains (dashed lines) in (II).

ring bond distances are, in general, not significantly different from those found in cytosine or cytosine monohydrate. In both structures, the cytosinium cation acts as a hydrogen-bond donor *via* its N and C atoms (N1, N2, N3, C4 and C5). The hydrogen sulfate H atom acts as an O—H···O hydrogen-bond acceptor (Tables 2 and 3).

In (I), the combination of H atoms of the amino group with two other different hydrogen bonds (N3—H3···O2 and C5—H5···O2) generates the same type of binary graph set, $R_2^2(8)\overrightarrow{c}\overleftarrow{d}$ and $R_2^2(8)\overrightarrow{e}\overleftarrow{f}$ (Grell *et al.*, 1999). The hydrogen-bonding binary graph set is essentially formed by infinite chains with a maximum degree of ten. The two types of rings observed in this graph are those cited below. The propagation

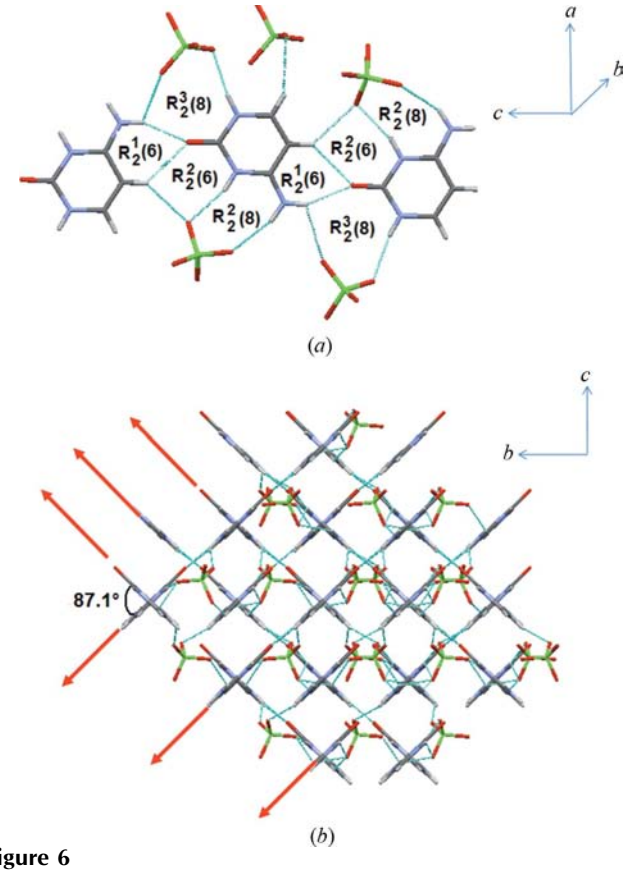

Figure 6
The hydrogen-bonding pattern in (II), showing (*a*) rings constructed from chains and (*b*) crossed layers generated by combination of the rings.

of these infinite chains, and their combination with rings formed by N2—H2N···O1 and C5—H5···O2 hydrogen bonds, generates chains of edge-fused $R_4^4(18)$ $\overrightarrow{b}\overleftarrow{c}\overrightarrow{e}\overleftarrow{b}\overrightarrow{d}\overleftarrow{f}$ rings running along [102] (Fig. 4*a*). These chains of rings are interlinked along [110] by mixed chains formed by the two binary rings $R_2^2(8)$ $\overrightarrow{c}\overleftarrow{d}$ and $R_2^2(8)$ $\overrightarrow{e}\overleftarrow{f}$ using H atoms of the amino group (see below). The combination of these three types of rings leads to layers which are stacked along [101]. The junction between these layers is ensured by the only O—H···O hydrogen bond present in the structure, for which the hydrogen sulfate anion is the donor and the cytosinium cation the acceptor (Fig. 4*b*). The structure of cytosinium hydrogen sulfate can thus be described as a succession of mixed layers parallel to their stacking direction [102], linked by strong O—H···O hydrogen bonds.

The structural integrity of (II) is maintained by a three-dimensional hydrogen-bonding network between cations, and between cations and anions. A very strong N3—H3···O4 hydrogen bond is observed. The cytosine cation is linked to a single perchlorate ion by N—H···O and C—H···O hydrogen bonds. All hydrogen bonds present in this structure are three-centred except N1—H1···O4 and C6—H6···O1. Cation–cation N—H···O and C—H···O hydrogen bonds present in this structure form two symmetrically crossed infinite chains of rings with an $R_2^1(6)$ $\overrightarrow{d}\overleftarrow{h}$ graph-set motif. These chains are crystallographically linked by the *a* glide plane, and the angle between them is about 87.1° (Fig. 6). The junction between the cationic chains occurs *via* the perchlorate anion as a result of cation–anion hydrogen bonds. The crystal structure is thus based on crossed mixed cation–anion layers in a three-dimensional hydrogen-bonded network. These layers are formed by rings of hydrogen bonds involving the terminal $-NH_2$ group, atoms N3 and C5 as donors, and O atoms as acceptors, to form chains of edge-fused rings $R_2^2(6)$ $\overrightarrow{f}\overleftarrow{g}\overrightarrow{h}$ and $R_2^1(6)$ $\overrightarrow{d}\overleftarrow{h}$ stacked along [021]. These chains are interlinked by $R_2^3(8)$ $\overrightarrow{a}\overleftarrow{e}\overrightarrow{d}$ and $R_2^2(8)$ $\overrightarrow{e}\overleftarrow{f}$ rings (Fig. 6*a*). Such rings are also found along [012], crossing the first sheet of chains of rings to form a three-dimensional hydrogen-bonded network; this can be understood as the result of the geometry of the perchlorate anion acceptor atoms (Fig. 6*b*).

In an attempt to study the influence of anion substitution (Fig. 7) on the graph-set analysis, we used the same three reactions, giving three similar products with three different anions.

The substitution of a tetrahedral hydrogen sulfate anion by a planar nitrate anion or a tetrahedral perchlorate anion does not affect the general packing features of the crystal structure. Indeed, the same mixed two-dimensional layers are observed in the two compounds. These layers are parallel to [102] in (I) and at an angle of 87.1° in (II). However, the difference in geometry between the two anions, and the absence of H atoms in the perchlorate anions, directly affect the hydrogen bonds in the two structures. The construction of hydrogen-bonding binary graph sets for the two compounds yields the same rings for the two crystal structures, with a variation in the degree *n*. However, in the case of (II), we observe an additional $R_2^1(6)$ ring. This additional binary graph set is generated by cytosinium–cytosinium hydrogen bonds and this is due to the absence of H atoms on the anion. The structures of the three cytosinium compounds can thus be described as two-dimensional mixed sheets formed by a succession of edge-fused $R_d^a(n)$ rings. The orientation of these sheets depends on the geometry of the acceptor atoms on the anion. In the hydrogen sulfate and nitrate anions, the geometry of the acceptor atoms is identical and the sheets have the same parallel orientation. However, the absence of an H atom in the nitrate anion makes its structure less compact than the others. This is due to the junction between the mixed layers, which is ensured by the strongest O—H···O hydrogen bond [O···O = 2.558 (3) Å] in cytosinium hydrogen sulfate, but by van der Waals interactions between the cations [3.09 (2) Å] in cytosinium nitrate. The tetrahedral geometry of the acceptor atoms of the perchlorate anion causes these sheets to be crossed at an angle of 86.91° 87.1°. In cytosinium nitrate and (II), which have no H atom in the anion, we observe interaction between the cytosinium cations; this interaction is not observed in (I) due to the presence of an H atom on the anion. The interactions observed between the two cations belonging to the same layer (C5···O5 = 3.965 Å and C6···O5 = 3.930 Å) in (I) are shortened, and they moderate the N—H···O hydrogen bonds in (II) [N2···O5 = 2.8473 (13) Å].

The crystal structures of the three cytosinium salts are thus similar and can be described as a succession of cation–anion mixed sheets held together by strong hydrogen bonds. The

study of anion substitution in these structures allows us to conclude that the geometry of the acceptor atoms and the presence or absence of H atoms in the anionic part directly affect the packing of sheets in the crystal structure, as well as the hydrogen-bonded graph-set pattern.

Experimental

The same crystallization method was used to prepare the three compounds, but in each case the acid was different: sulfuric acid for (I), perchloric acid for (II) and nitric acid for cytosinium nitrate. The experiment consists of heating an equimolar solution of cytosine and mineral acid until the reaction is complete. Colorless crystals were obtained by evaporation of the solution at room temperature over the course of a few weeks.

Compound (I)

Crystal data

$C_4H_6N_3O^+\cdot HSO_4^-$
M_r = 209.19
Monoclinic, *Cc*
a = 14.676 (2) Å
b = 7.435 (2) Å
c = 7.574 (2) Å
β = 111.79 (2)°
V = 767.4 (3) Å^3
Z = 4
Mo *K*α radiation
μ = 0.42 mm^{-1}
T = 120 K
0.4 × 0.3 × 0.2 mm

Data collection

Nonius KappaCCD area-detector diffractometer
5769 measured reflections
2422 independent reflections
2024 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.091
S = 0.91
2422 reflections
134 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Absolute structure: Flack (1983), with 1410 Friedel pairs
Flack parameter: 0.59 (8)

Compound (II)

Crystal data

$C_4H_6N_3O^+\cdot ClO_4^-$
M_r = 211.57
Orthorhombic, $Pca2_1$
a = 17.194 (2) Å
b = 4.940 (1) Å
c = 8.901 (1) Å
V = 756.1 (2) Å^3
Z = 4
Mo *K*α radiation
μ = 0.50 mm^{-1}
T = 100 K
0.3 × 0.2 × 0.09 mm

Data collection

Nonius KappaCCD area-detector diffractometer
11932 measured reflections
2198 independent reflections
2146 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.055
S = 1.06
2198 reflections
130 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983), with 1166 Friedel pairs
Flack parameter: 0.02 (4)

Table 1
Comparison of bond lengths and angles in the cytosinium cation of (I) and (II) (Å, °).

Bond	(I)	(II)	Angle	(I)	(II)
O5—C2	1.236 (3)	1.2184 (13)	C2—N1—C6	122.0 (2)	123.00 (9)
C4—N2	1.318 (3)	1.3119 (14)	C2—N3—C4	124.42 (18)	124.84 (9)
C4—N3	1.358 (2)	1.3629 (13)	O5—C2—N3	119.7 (2)	120.77 (9)
C4—C5	1.417 (3)	1.4237 (14)	O5—C2—N1	124.2 (2)	124.28 (9)
N3—C2	1.371 (3)	1.3847 (12)	N1—C2—N3	116.06 (19)	114.95 (9)
C5—C6	1.346 (3)	1.3533 (14)	N2—C4—N3	118.08 (17)	119.33 (9)
N1—C6	1.369 (3)	1.3624 (14)	N2—C4—C5	124.23 (16)	123.26 (9)
N1—C2	1.354 (3)	1.3629 (13)	N3—C4—C5	117.7 (2)	117.42 (9)
			C4—C5—C6	118.1 (2)	118.23 (9)
			N1—C6—C5	121.7 (2)	121.54 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.856 (17)	2.023 (18)	2.872 (3)	172 (3)
N2—H1N···O3^{i}	0.87 (2)	2.15 (2)	3.007 (3)	172 (3)
N2—H1N···O4^{ii}	0.87 (2)	2.53 (3)	2.914 (4)	107.8 (17)
N2—H2N···O1^{iii}	0.860 (17)	2.13 (2)	2.966 (3)	163 (3)
N3—H3···O2^{i}	0.872 (17)	1.835 (17)	2.701 (3)	172 (2)
O4—H4···O5^{iv}	0.86 (2)	1.71 (2)	2.558 (3)	168 (3)
C5—H5···O2^{iii}	0.95	2.33	3.252 (3)	165

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

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	0.862 (11)	2.037 (11)	2.8892 (11)	169.4 (13)
N2—H1N···O1	0.857 (13)	2.272 (14)	3.0286 (13)	147.4 (13)
N2—H1N···O3^{ii}	0.857 (13)	2.484 (14)	3.0830 (12)	127.6 (12)
N2—H2N···O2^{iii}	0.864 (14)	2.513 (15)	2.9229 (13)	110.0 (12)
N2—H2N···O5^{iv}	0.864 (14)	2.042 (14)	2.8473 (13)	154.8 (14)
N3—H3···O4	0.863 (13)	2.030 (13)	2.8764 (12)	166.5 (13)
C5—H5···O4^{iv}	0.95	2.42	3.1827 (13)	137
C5—H5···O5^{iv}	0.95	2.37	3.1069 (13)	134
C6—H6···O1^{v}	0.95	2.53	3.3298 (13)	142

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

All H atoms were located in difference electron-density maps. All H atoms attached to C atoms were treated as riding, with C—H = 0.95 Å (aromatic) and U_{iso}(H) = 1.2U_{eq}(C). The positions of H atoms attached to N or O atoms were refined freely, with U_{iso}(H) = 1.2U_{eq}(N,O). For cytosinium hydrogen sulfate, (I), the measured crystal was an inversion twin with an approximate twin ratio of 0.6:0.4 [Flack (1983) parameter = 0.59 (8)].

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *PLATON* (Spek, 2009) and *Mercury* (Version 1.4; Macrae *et al.*, 2006) for (I); *WinGX* (Farrugia, 1999) for (II).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BD3008). Services for accessing these data are described at the back of the journal.

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